THE IMPORTANCE OF THIOSALT SPECIATION IN THE MANAGEMENT OF TAILING PONDS

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The importance of thiosalt speciation in the management of tailing ponds

by

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ABSTRACT

The presence of thiosalts in mining wastewaters is an environmental issue due to the resulting pH depression as these species degrade with time. Despite research in the area, reaction kinetics of thiosalt species under different pH and temperature conditions are not fully understood, especially in conditions common in receiving ponds. As a result, it is difficult to design ponds or develop treatment technologies to treat these compounds. Several studies have dealt with the reaction kinetics of major thiosalt species (thiosulfate, trithionate, tetrathionate) under various pH and temperature conditions. However, further research is required to better understand the fundamental behaviors of thiosalt species and identify probable reaction paths in temperatures below 30 °C, pH range between 2 and 9 and in the presence of reagents.

The overall objectives of this work have been to study the behavior of thiosalts in mining wastewaters and develop a model of their behavior under the conditions studied that includes pH and temperature as independent variables. The study is divided in four parts: the first part is a summary of relevant information in terms of generation and kinetics of thiosalts, analytical methods for measuring their concentrations, and treatment of thiosalt wastes. Despite extensive research in the area, generation and kinetic information of thiosalt species under different pH and temperature conditions is not fully understood, especially under the range of conditions likely to be encountered in receiving ponds.

The second part of the study analyzes the behavior of thiosulfate, trithionate and tetrathionate and provides with mathematical models for their behavior as pure species under the specified conditions. The third part of the study consists of the analysis of the thiosalt behavior in mixtures following a decoupling approach; this analysis provided with additional information for the proposal of global reaction pathways for the species. Finally, the last chapter provides preliminary results from kinetic experiments with selected reagents, results from equilibrium

simulations and an analysis of future work required to improve the understanding of thiosalt reactions, improve treatment efficiency and reduce the environmental impact of acid mine drainage.

ACKNOWLEDGEMENTS

I would like to thank my supervisor Dr. Kelly Hawboldt for the opportunity to work with her in this project. Her guidance and support were outstanding and allowed me the freedom to make this a very positive, professional and personal, experience. I would also like to thank the rest of my committee, Dr. Christina Bottaro and Dr. Faisal Khan, for their support, guidance and patience during all these years.

During my work, I had the opportunity to share my time here with outstanding researchers and professionals that helped me along the way including Dr. Geert Van Biesen, Dr. Robert Helluer, Ms. Marsha Roche, PhD Candidate John Halfyard, Ms. Rachel Moores and Ms. PunjamaJayasinghe. I would also like to recognize my friends, coaching colleagues and Bitter's workmates that helped me stay away from the office and lab long enough to stay mentally sane. I would also like to thank Dr. Thomas Humphries for his valuable help in the development of the Matlab models and the good discussion about regressions and soccer.

Special thanks to PhD candidate Michael Pappoe, this work was possible in part thanks for his dedication and support during the analytical part of the research. We also had our share of frustrations with the CE, but at the end it was part of the learning process. In addition, I would also like to recognize the previous work done by YaovalukVongporm at Memorial University which served as background of the presence work.

Last, I would like to thank my wife, Bethel, for all her support and encouragement during the four years of the program. The completion of this journey would not be possible without her love, courage and dedication to our kids. She was the cornerstone in this adventure and I am sure she will be pleased not be married to a student anymore.

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List of Symbols, Nomenclature or Abbreviations

°	degree
μ	micro
ΔG	Gibbs free energy
AMD	Acid mine drainage
CE	Capillary Electrophoresis
DTA	Differential thermal analysis
EC50	Half maximal effective concentration
Fmincon	Matlab command
Hr	hours
IC	Ion Chromatography
K	Reaction constant
LC	Liquid Chromatography
M	moles per liter
mL	milliliters
ODE	Ordinary Differential Equation
ODE45	Matlab command
ppm	parts per million
T	temperature

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Introduction

Thiosalts are sulfur compounds generated in mining and metal processing operations (Dinardo and Salley, 1998) or naturally in the presence of Fe^{III}(Kuyucak et al, 2001). These species, also known as polythionates, are intermediates in the oxidation of sulfide (S_2^{2-}) to sulfate (SO_4^{2-}). Based on their stability, the most important species are: thiosulfate ($S_2O_3^{2-}$), trithionate ($S_3O_6^{2-}$) and tetrathionate ($S_4O_6^{2-}$) (Brimblecome, 2005, Dinardo and Sally, 1998; Kuyucak et al, 2001; Vongporm, 2008). Although these compounds are not considered toxic, their presence in the environment can accelerate environmental problems such as acidification of water bodies and promotion of metal migration from soil and sediment (Kuyucak et al, 2001).

In recent years, thiosulfate has been studied as a substitute for cyanide in the recovery of silver and gold (Ahern et al., 2006; Senanayake, 2007; Zhao et al. 1999). Thiosalts in the mining/metal processing effluents result from oxidation processes associated with the unit operations (Chanda and Rempel, 1987; Kuyucak et al., 2001). Factors that affect the production of thiosalts in such processes are ore characteristics (such as amount and species of sulfur), process pH and temperature, residence time, pulp density, and chemicals used in the process, among others (Kuyucak et al., 2001; Dinardo and Sally, 1998). Although the amount of thiosalts produced will vary according to the process, the concentration in the effluent could be as high as 1200 ppm (Dinardo and Sally, 1998; Kuyucak et al, 2001; Rolia and Tan, 1985). Once the thiosalts are produced, they usually pass through different water treatment processes without any significant oxidation. However, once in the receiving pond, several factors promote the oxidation of thiosalts to sulfate such as the presence of *Thiobacillus* bacteria in natural environments, seasonal pH shifts that occur in the ponds (Dinardo and Sally, 1998), and presence of chemical catalysts (Druschel et al, 2003b).

The lack of appropriate treatments technique and the pH depression caused by the oxidation of the thiosalts have made them subject to extensive studies to identify their origin in the mining process (Kuyucak et al, 2001; Rolia and Tan, 1985) and their kinetic behavior under different conditions (Ahern, 2006; Meyer and Ospina, 1982; Mizoguchi et al, 1976; Rolia and Chakrabarti, 1982; Suzuki, 1999; Xu and Schoonen 1995).Based on the previous studies, this research has the following objectives: identify reaction mechanisms of thiosulfate, trithionate and tetrathionate under different pH and temperature conditions; develop mathematical models to predict thiosalt behavior in pond conditions as pure species and mixtures and finally, propose global reaction mechanisms. Each sample point was taken at least three times with a few exceptions where only two samples were taken at specific conditions of the experiments. The experimental error calculated for thiosalt replications in the capillary electrophoresis were 8%, for thiosulfate, 10% for trithionate and 9% for tetrathionate. The origin of these errors is expected to be in mainly in sample management (fast-freezing/thawing of samples) and measurements in balances and other analytical equipment.

The document is divided in four chapters; the first chapter is a review paper done in the topic, which outlines work done in the area for the previous 25 years and set up the bases for the study. The second chapter provides the analysis of thiosulfate, trithionate and tetrathionate as pure species in the selected conditions in the lab. In this chapter, the rate equations for individual species are presented as well as the global reaction pathways. After proposing the individual rates and pathways, the analysis moves into the behavior of mixtures, using a decoupling approach, which is presented in chapter three. Chapter four presents preliminary results thiosalt's behavior under selected reagents as well as an equilibrium analysis under potential reagents present in the pond. In this chapter, the path forward in the research related to thiosalts in tailing ponds is proposed.

Co-authorship Statement

The nature of this research is interdisciplinary and required collaboration between researchers of different areas, especially chemistry and engineering. In all of the papers presented in the following chapters, I, J. Clemente Miranda-Trevino, am the principal author with support and guidance of my supervisors Dr. Kelly Hawboldt and Dr. Christina Bottaro.

For all of the chapters, I was responsible for the development of the manuscript, its organization and preparation.Data used in the determination of the kinetic information via the initial rate method was gathered by me and confirmed using data obtained by Vongporm (2008) in a previous study done at the University. This data was also partially used in Chapter 3 for the development of mixture reaction rates.

The only exception in the document is chapter 1 section 2 "Analytical methods for detection and quantification of thiosalts". Mr. Michael Pappoe prepared this section as part of the review process in thiosalts. In addition, Mr. Pappoe developed the analytical method used to determine the concentration of thiosalts in solution.

Chapter 1

The importance of thiosalts speciation: review of analytical methods, kinetics and treatment

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1. Introduction

Thiosalts, also known as polythionates, are sulfur oxyianion compounds. The concentration of the thiosalts formed correlates with the percent of sulfide in the ore as well as conditions such as temperature and exposure to oxidizing environments (Dinardo and Sally, 1998). The general structure is $S_nO_m^{2-}$ and the most important species from an acid mine drainage (AMD) perspective are thiosulfate ($S_2O_3^{2-}$), trithionate ($S_3O_6^{2-}$) and tetrathionate ($S_4O_6^{2-}$).(Figure 1)

Thiosulfate Trithionate Tetrathionate

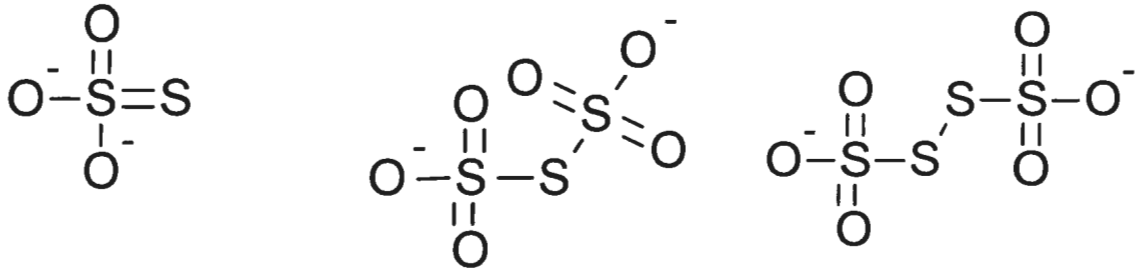


Figure 1 Thiosalt structures

Thiosalts species are typically intermediate sulfur species similar to sulfur intermediates such as sulfites, bisulfites and polysulfides (Dinardo and Sally, 1998). The reactivity of thiosalts is complex and strongly dependent on temperature, pH, and oxygen as well as the presence of other thiosalts, metals and microorganisms. At typical tailing pond conditions according to thermodynamic equilibrium calculations, most sulfur compounds

oxidize to sulfate, however, partially oxidized species, such as thiosalts, occur in the mining effluent due to limits imposed by mass transfer and kinetics (Wasserlauf and Dutrizac, 1982).

Thiosalts are generated during the milling and flotation of sulfide ores, particularly those containing pyrite (FeS_2) and those pyrrhotitic-rich (Negeri et al., 1999). Over time (depending on species and conditions) thiosalt oxidation leads to pH depression (acidification) of the receiving water bodies such as lakes and rivers. In addition, thiosalts in the flotation process have also been shown to reduce the overall effectiveness of the mineral collector used in the process (Ramachandra, 2006).

1.1 Thiosalt generation

Thiosalts are naturally present in volcano crater lakes and in run-off from excavated sites that contain sulfur and sulfur–metabolizing bacteria. (Briblecome, 2005; Sriwana et al., 2000; Takano et al., 1994). They are also common intermediates in the oxidation of pyrite, which is the most common sulfide mineral on earth (Bernier, 2007; Schippers et al., 1996b; Sasaki et al., 1995; Paschka and Dzombak, 2004; Johnson, 2003). Thiosalts are also naturally formed in volcanoes and serve as an indicator of their activity (Takano et al., 1994). In crater lakes, polythionates are generated by the reactions between hydrogen sulfide and sulfur dioxide (Swirana, 2000). The main species are $S_4O_6^{2-}$, $S_5O_6^{2-}$, $S_6O_6^{2-}$ (Briblecome, 2005); their presence is linked to the presence of bacteria and microorganism in the volcanic environment. Polythionates in run-off from volcanoe craters have similar effects to AMD, as thiosalt concentrations can reach up to 1900 ppm.

The reactivity of pyrite in tailings and in processing has been widely studied (Borda et al., 2004; Chernychova, 2003; Goldhaber, 1983; Mckibben, 1994; Moses et al., 1987; Rimstidt and Vaughan, 2003 Schippers et al., 1996b). Conditions such as pH of the solution, dissolved oxygen concentration, ferric and ferrous ion concentrations, the presence of other sulfur intermediates and the presence of bacteria such as

Thiobacillusferroxidans and *Leptospirillumferrooxidans* will affect the oxidation of pyrite (Moses et al., 1987; Parschka, 2004; Shippers, 1996a).Pyrite oxidation occurs via two major oxidants (Borda et al., 2004; Johnson, 2003, Sasaki et al., 1995): Ferric ion (i.e. Fe^{3+}) and oxygen (O_2). Several studies indicate that ferric ion is the main oxidant at low pH (Borda et al., 2004; Parshka, 2004; Johnson, 2003; Sasaki et al., 1995; Moses et al., 1987) while oxygen is more important at neutral pH (Parschka, 2004) according to the following overall reactions:

$$FeS_2 + 14\ Fe^{3+} + 8\ H_2O \rightarrow 15\ Fe^{2+} + 16\ H^+ + 2\ SO_4^{2-} \quad (1)$$

$$FeS_2 + 3.5\ O_2 + H_2O \rightarrow Fe^{2+} + 2\ H^+ + 2\ SO_4^{2} \quad (2)$$

Pyrite oxidation is a complex process and products will depend on the conditions of the solution. Figure 2 shows a general oxidation pathway for pyrite, which has been reported for low pH conditions (Druschel, 2004):

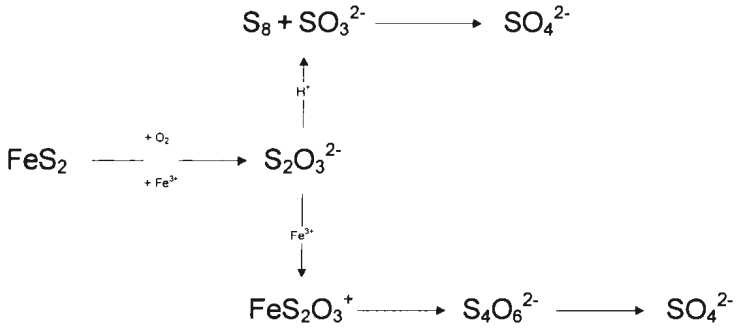


Figure 2 Oxidation pathways for pyrite (Modified from Druschel et al., 2004).

Several authors identified thiosulfate as the first thiosalt product of pyrite oxidation (e.g. Borda et al., 2004; Chernychova, 2003; Druschell et al., 2004; Moses et al., 1987; Moses and Herman, 1990; Sasaki et al., 1995), the proposed mechanism for this reaction is as follows (modified from Rimsdidt, 2003):

$$FeS_2 \rightarrow FeS_2^{+} + e^{-} \quad (3)$$

$$FeS_2^{+} + H_2O \rightarrow FeS_2OH + H^+ \quad (4)$$

$$FeS_2OH \rightarrow FeS_2O + e^{-} + H^+ \quad (5)$$

$FeS_2O \rightarrow FeS_2O_2 + 2e + 2H^+$ (6)

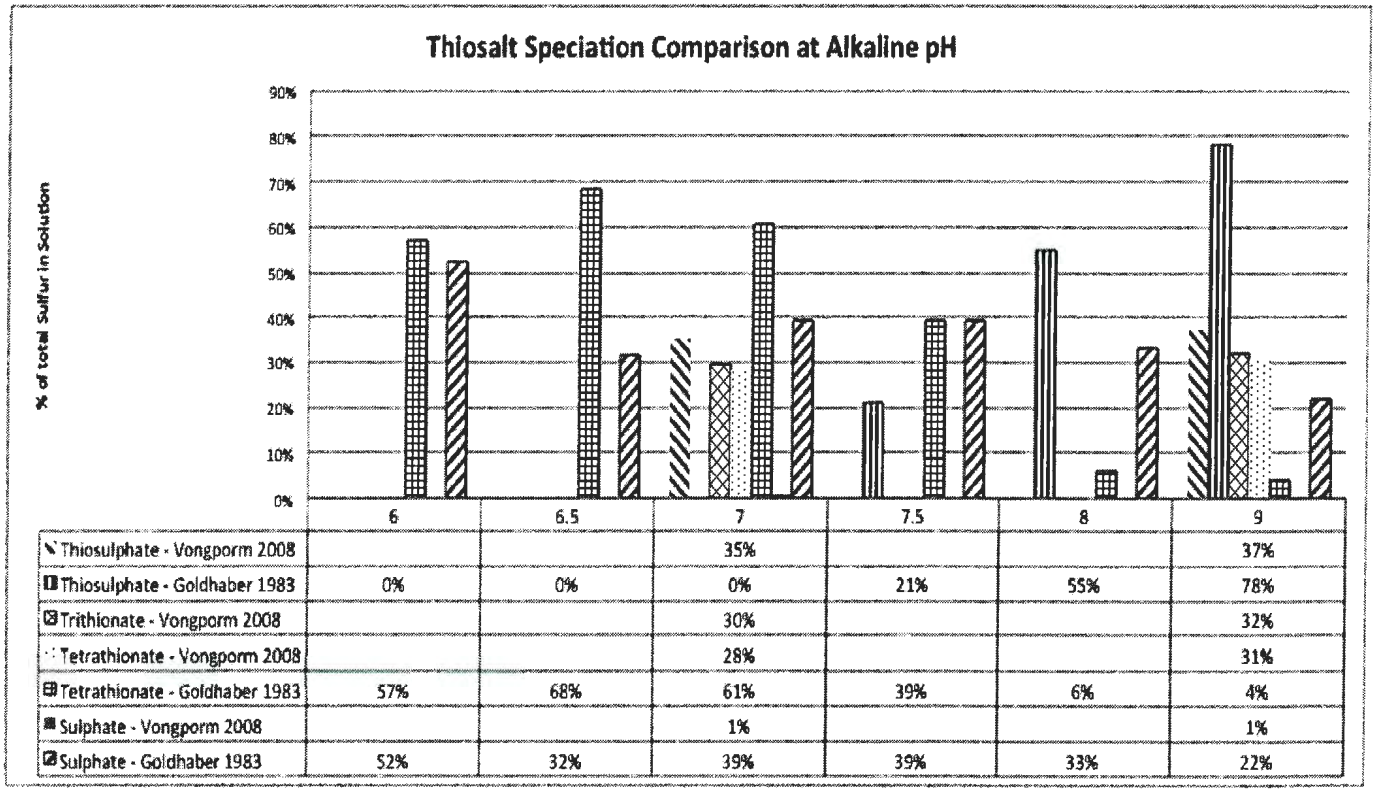
$FeS_2O_2 \rightarrow FeS_2O_3 + 2e^- + 2H^+$ (7)

$FeS_2O_3 \rightarrow FeS_2 + S_2O_3^{2-}$ (8)

Other sulfur species resulting from pyrite oxidation are trithionate ($S_3O_6^{2-}$), tetrathionate ($S_4O_6^{2-}$) and sulfate (SO_4^{2-}) as shown in Figure 3 (Williamson and Rimstidt, 1992). It is difficult to use thiosulfate as a reaction progress indicator due to its reactivity under acidic conditions. For example, Schippers et al. (1996a) and Steudel (1996) identified thiosulfate, as the key product in pyrite oxidation but under acidic conditions thiosulfate will react to tetrathionate according to the following:

$2\ S_2O_3^{2-} + 2\ Fe^{3+} \rightarrow FeS_2O_3^{+} + FeS_2O_3^{+} \rightarrow 2Fe^{2+} + S_4O_6^{2-}$ (9)

$2\ S_2O_3^{2-} + \frac{1}{2}\ O_2 + 2H^+ \rightarrow H_2O + S_4O_6^{2-}$ (pyritecatalyzed) (10)



	6	6.5	7	7.5	8	9
Thiosulphate - Vongporm 2008			35%			37%
Thiosulphate - Goldhaber 1983	0%	0%	0%	21%	55%	78%
Trithionate - Vongporm 2008			30%			32%
Tetrathionate - Vongporm 2008			28%			31%
Tetrathionate - Goldhaber 1983	57%	68%	61%	39%	6%	4%
Sulphate - Vongporm 2008			1%			1%
Sulphate - Goldhaber 1983	52%	32%	39%	39%	33%	22%

Figure 3 Percentage of S speciation from pyrite oxidation according to the pH of the solution (modified from Goldhaber, 1983) and S speciation from pure thiosalt species according to the pH only (Vongporm, 2008)

Several studies (e.g. Kuyucak, 2001; Negeri et al., 1999; Rolia, 1985; Wasserlauf and Dutrizac, 1982) have identified key factors in the generation of thiosalts in the mining process such as sulfur content in the ore, grinding and flotation pH, grind size, residence time in the mill, pulp agitation rate, temperature, SO_2 addition, dissolved oxygen in grinding solution, air flow in flotation and chemicals used in the system. The conditions in grinding and flotation units play an important role in thiosalt generation, as factors such as temperature, residence time and pH have a linear effect on the production of thiosalts in the process (Negeri et al., 1999).

Negeri et al., (1999) studied two types of ores at lab scale to determine where in the mining process thiosalts are generated. The grinding of dry pyrrhotitic ores and processing through the copper circuit (as shown in Figure 4) generates higher amounts of thiosalts than these same processes applied to pyritic ores. There is a linear relationship between the amount of sulfide present in the ore and the total thiosalts produced in the process. Key factors in thiosalts production in pyritic ore processing are pH and grinding media, while for pyrrhotitic ore temperature and residence time dominate. The pH range that favors the generation of thiosalts is 9.4 to 10.7; over that range, thiosulfate generation dominates over polythionates (Rolia and Tan, 1985; Wasserlauf and Dutrizac, 1982). In the grinding circuit, a pH close to neutral will inhibit the generation of thiosalts, where the dominant species are thiosulfate and trithionate.

The average generation of thiosalts for each ore in the process is shown in Figure 4.

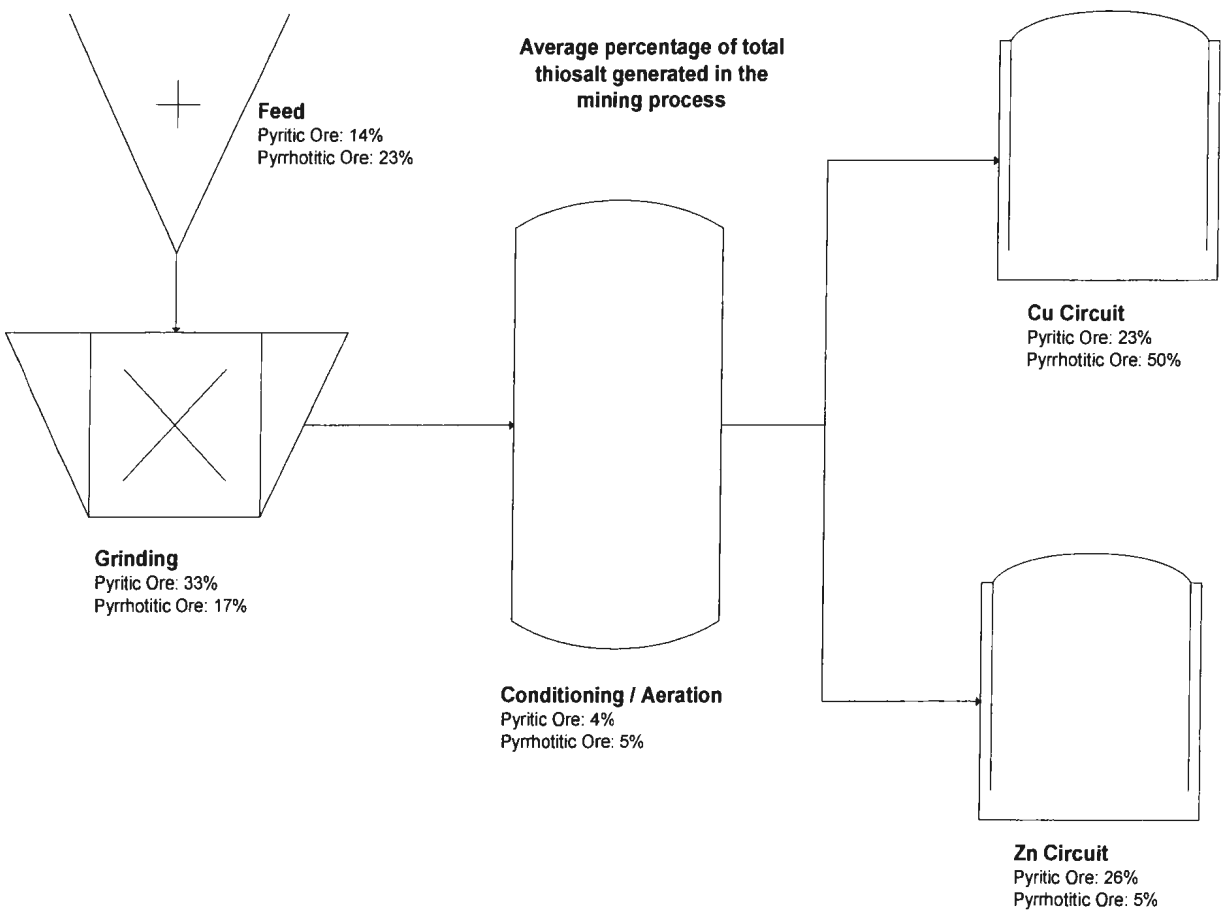


Figure 4 Average percentage of total thiosalt generated in the mining process (modified from Negeri et al. 1999).

In acidic and weakly alkaline media, sulfur is metastable, hence the formation of thiosalts is limited; however, the presence of SO_2, in unit operations of the mining process at a pH above 8, oxidizessulfur to thiosulfate. The main species generated are thiosulfate, trithionate and tetrathionate (Rolia and Tan, 1985). Other factors that impact the generation are the reagent used to control pH - lime generates less thiosalts than soda ash and the grinding media (steel rods or stainless steel rods) (Negeri et al., 1999; Kuyucak, 2001; Rolia and Tan, 1985). Unlike in the grinding process, the pH is not relevant for the formation of thiosalts during the flotation circuit. At this stage, the agitation and resident time play a more important role (Kuyucak, 2001). In addition to the generation of thiosalts in the process, thiosulfate can be used instead of cyanide for the extraction of gold from ore (Senanayake, 2007).

1.2 Thiosalts and Acid Mine Drainage (AMD)

Acid mine drainage (AMD) is the term used to identify the water coming from the mining process combined with the rainfall and snowmelt that leach from the waste pile (Kuyucak, 2006). Mine water is not only produced during the active life of the mine but also after the closure of the site (Johnson, 2003). The oxidation of residual sulfur ores in the mine and residue and ore in dumps has been identified as one of the key precursors of acid mine drainage (AMD) which can lead to environmental problems such as metal leaching, precipitation and generation of acidic water (Druschel et al, 2004; Johnson, 2003; Tiwary, 2001). During the sulfur oxidation former process, thiosalts play an important role in the generation of protons that decrease the pH of the watersheds. An overall pathway is outlined in Figure 5.

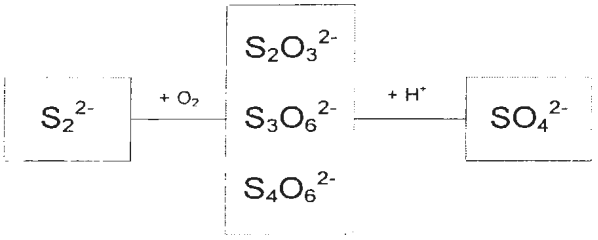


Figure 5 General reaction pathway of sulfide oxidation (Suzuki, 1999)

Factors that influence the generation of AMD include presence and species of microorganisms and dissolved oxygen (Kalin et al., 2006; Vigneault et al., 2001; Perez-Lopez et al., 2007; Johnson, 2003, Norlund et al. 2009). General characteristics of AMD are acidic pH (~2), high sulfate concentration and high metal loading, especially iron (Tiwary, 2001).

Figure 6 shows a summary of the prevention and remediation techniques used in the treatment of AMD. Prevention strategies have two objectives: The reduction of oxygen available to tailings and the inhibition of Fe-oxidizing bacteria (Vigneault et al., 2001).

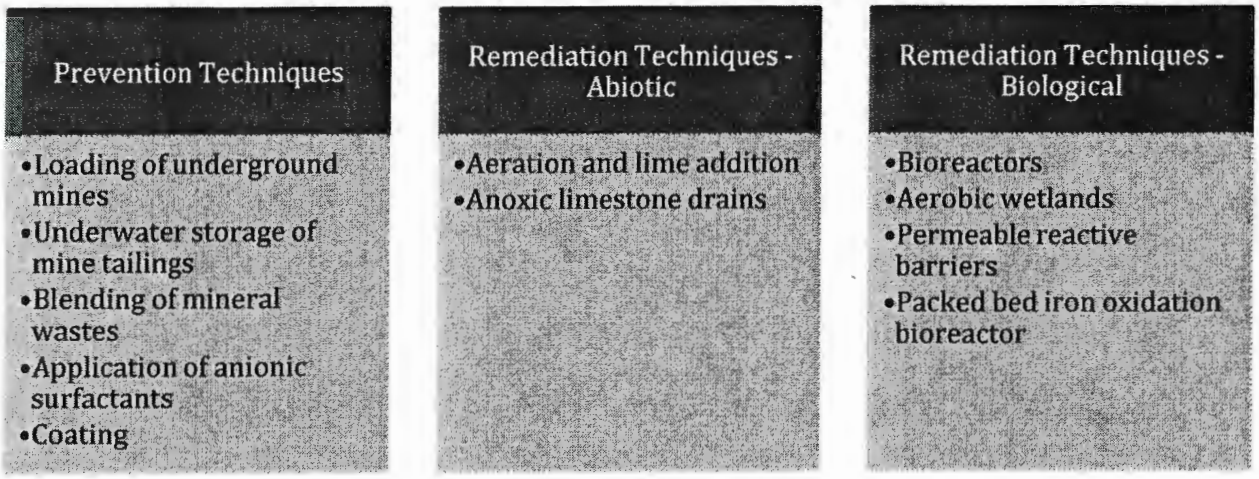


Figure 6 Prevention and Remediation Techniques for AMD (Modified from Johnson, 2003).

The techniques shown in Figure 6 do not consider the generation and reactivity during the process or tailing ponds but rather focus on inhibiting the oxidation of the sulfur ores or in the case of the remediation techniques, enhancing this oxidation prior to the disposal of the water. As a result, a large source of AMD in the form of thiosalts is not managed in prevention or treatment methods. Typical levels of thiosalts are outlined in Table 1. The calculated pH depression if all thiosalts oxidize is also summarized in this table.

Table 1 Typical thiosalt concentrations and pH depression generated (Rolia and Tan, 1985)

Site (location)	Thiosalt concentration (ppm)	pH units generated by thiosalt oxidation
Canmet Development Mill	500	~ 5.0
Heath Steele (NB)	440	~ 5.0
Brunswick Mining (NB)	1900	~ 5.5

1.3 Thiosalt speciation relevance

The relevance of thiosalt speciation was identified by Wasserlauf and Dutrizac (1982) in their review of the topic. This paper presented analytical techniques, sampling and storage challenges as well as treatment technologies for thiosalts. The main reactions for each species were identified, however, the conditions reviewed were typically high temperature and pressure. Prior to this comprehensive review, there were other studies related to thiosalts that added insight about the reactions pathways and kinetics; for example, Mizoguchi et al. (1976) studied the disproportionation pathways for thiosulfate, trithionate and tetrathionate at temperatures of 70, 90, 110 and 130°C and identified the main products of oxidation.

Most studies in the early eighties focused on high temperatures (70 to 150°C) and often included only two thiosalt species; fewer studies included more species of thiosalts. For example, Meyer and Ospina (1982) studied the oxidation of thiosulfate and tetrathionate at temperatures from 20 to 70°C in mild acidic conditions (pH=3.5-4.0) and proposed reaction rates at the different temperatures (their results are discussed in later sections). Rolia and Chakrabarti (1982) studied thiosulfate, trithionate, and tetrathionate at pH above 10 and derived reaction constants and orders at temperatures between 70 to 85°C.

Rolia and Tan (1985) reported one of the first studies in thiosalt generation in processing mills from sulfide ores. However, despite identifying the presence of different thiosalts species, the study only included total thiosalt generation in different unit operations and process conditions, hence it is not possible to determine what the effects are of the different process conditions in the speciation of thiosalts. Starting in the middle of the 1990s, studies on thiosalts focused on specific species rather than on total thiosalts (i.e. Gould et al., 2004; Miranda-Trevino et al., 2009; Schippers et al., 1996a; Xu and Schoonen, 1995). Vongporm (2008) addressed the importance of thiosalt speciation in solution, identifying the different conditions under which the

compounds are reactive. These selected conditions of pH and temperature and the reactive thiosalt species are shown in Figure 7.

The number of thiosalt studies has increased due to increasing insight on the effects of pH and temperature on thiosalts species and speciation. Zhang and Dreisinger (2002) and Breuer and Jeffrey (2004) studied the effect of tetrathionate in gold leaching processes while Ahern et al. (2006) studied trithionate. Although the focus of the studies was process improvement, both papers provided useful information about the kinetics of tetrathionate oxidation in alkaline media at relatively low temperatures (22-40°C).

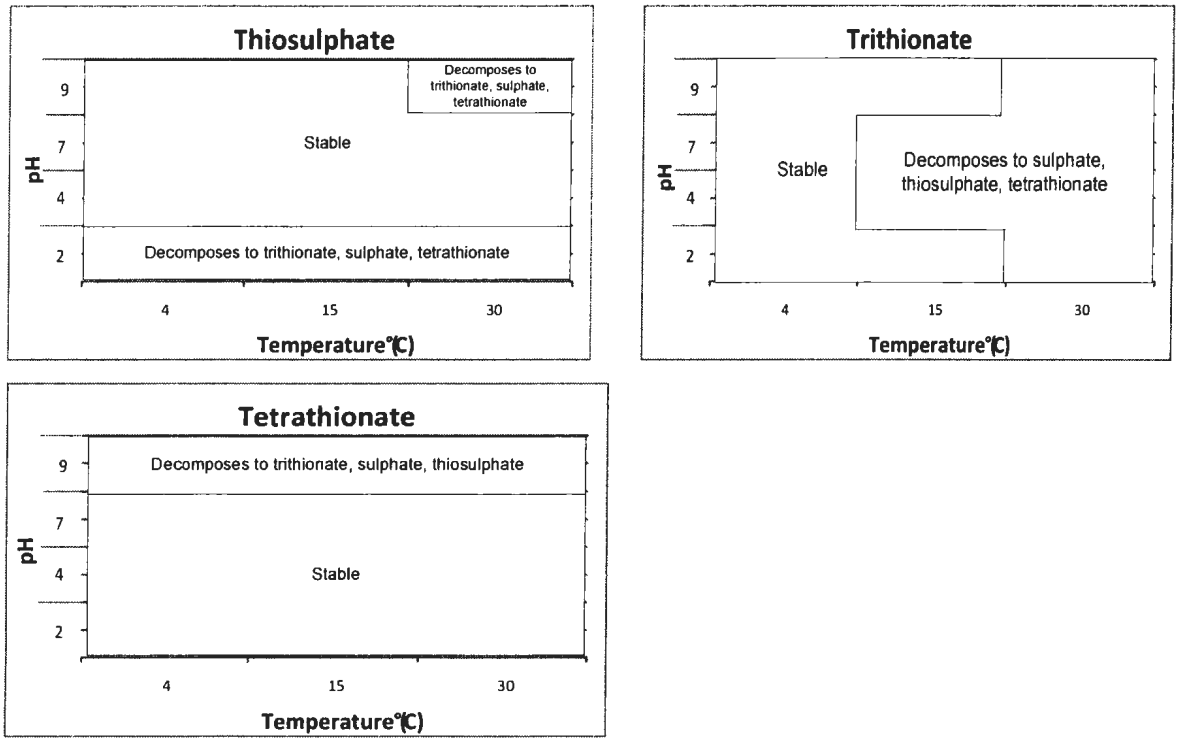


Figure 7 Reactive conditions for thiosalts (Modified from Vongporm, 2008)

Schippers et al. (1996a) analyzed the effect on mine waste degradation by bacteria. In the paper, the speciation of thiosalts and their behaviour under different pH conditions and in the presence of microorganisms are presented.However, the main objective of the study was to determine key inhibitors to bacterial activity and limiting the amount of

acid mine drainage generated. Another comprehensive study with microorganisms such as *acidithiobacillusferroxidans* and *acidithiobacillusthiooxidans* is by Bernier and Warren (2007) where kinetic information of thiosulfate and tetrathionate is presented. Bernier and Warren (2007) also follow up the changes in pH as a result of the microorganism oxidation and how the different bacteria changed the speciation in the solution.

An extensive and updated review of treatment options for thiosalts is presented by Dinardo et al. (1998) where an economical evaluation of each treatment is presented. In this review, most of the treatment options evaluated are exclusively for thiosulfate; though for treatment with hydrogen peroxide the speciation of thiosulfate, trithionate and tetrathionate is taken into account. There is a notable lack of information on the effect of speciation on treatment technologies under different pH and temperature conditions.

Species reactivity/stability is a function of pH and temperature and other reagents that promote or inhibit further oxidation or alter reactions pathways (Figure 7). Key to determining thiosalt reactivity and stability is accurate, reliable determination methods. Haddad (1997) presented the first study comparing results between ion chromatography (IC) and capillary electrophoresis (CE) for thiosalts. Furhter studies (Pobozy et al., 2002; Padarauskas et al., 2000; Motellier and Descostes, 2001) explored the advantages of the CE and developed methods for the different species which are presented in Section 2 of the paper.

1.4 Thiosalt toxicity

Thiosalts have a low toxicity compared to other substances (such as zinc and copper) under metal mining effluent regulations (MMER), with thiosulfate typically more toxic than tetrathionate (Table 2). Table 2 shows the reported IC25 (sublethal toxicity) or EC50 (acute toxicity) for thiosulfate and tetrathionate. Schwartz et al., 2006 and Yaschyshyn, 2006 concluded that the thiosalts concentrations typically found in the mining effluent did not have an acute impact on the reference organisms (Rainbow trout

and Daphnia Magna), though as can be seen in Table 1, environmentally relevant concentrations do occur in some mine effluents.

Table 2 IC25 or EC50 toxicity values for some thiosalts and selected metals (Schwartz et al. 2006; Toussaint et al. 1995; Brown 1968)

MMER Toxicity Test		Thiosulfate (mg/L)	Tetrathionate (mg/L)	Cu (mg/L)	Zn (mg/L)
Acute Toxicity Test (EC50)	Rainbow Trout	>819	>742	0.4	2.8
Sublethal Toxicity Test (IC25)	Duckweed (dry weight)	498	>798	--	--
	Duckweed (frond count)	525	>798	--	--
	Ceriodaphniadubia	59	562	0.027	0.076
	Fathead minnow	665	>891	0.48	2.65

However, pH depression as a result of thiosulfate and tetrathionate oxidation with concentrations around 160 ppm, has been shown to cause mortality in aquatic species such as Daphnia *Magna* (see Figure 8).

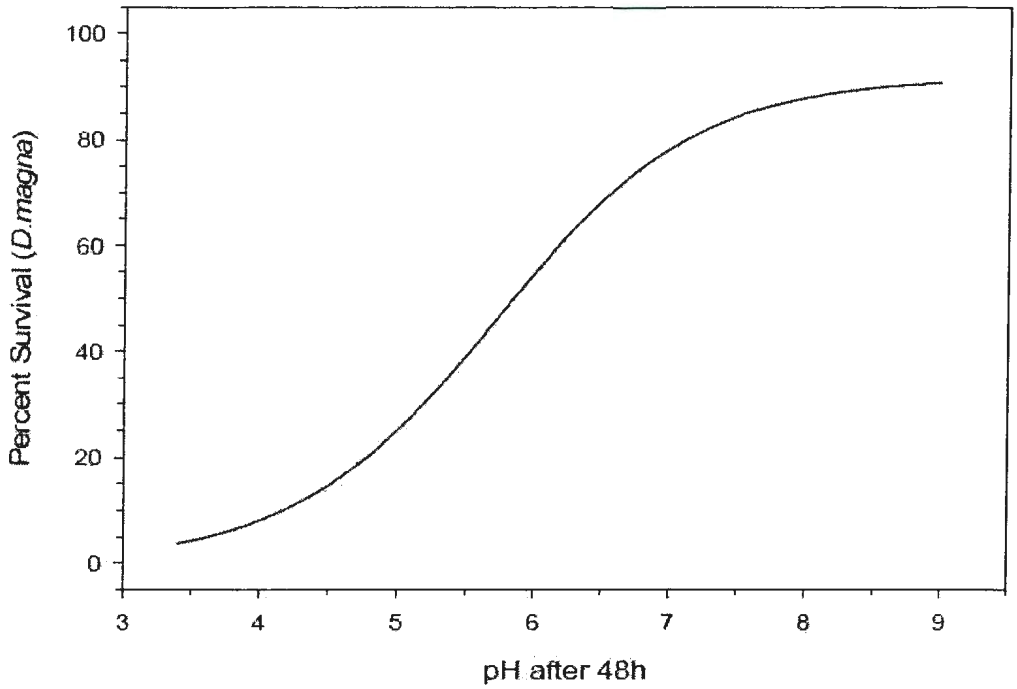


Figure 8 Trend for Daphnia Magna survival as result of pH change (modified from Schwartz et al. 2006)

Although there is some data on the toxicity of thiosalts, as presented in Table 2, in general this information is very limited. Furthermore, studies on the direct and indirect toxicity of thiosalts do not show a correlation between concentration and mortality of the species in the study (Holtze, 2010). The general consensus is that thiosalts are not directly acutely toxic at concentrations in mining effluents but rather indirectly due to potential pH depression, if they are present in solution (Schwartz, 2006; Vigneault et al., 2001; Holtze, 2010). Studies by Schwartz (2006) show that concentrations of up to 4100 ppm of thiosulfate do not show acute toxicity to rainbow trout, however when the pH of the solution dropped below 5 there was toxicity.

There are a number of issues that must be elucidated to determine thiosalts chronic toxicity such as reactivity/stability, behavior in AMD and methodologies to accurately measure thiosalts species.

2. Analytical methods for detection and quantification of thiosalts

2.1 Introduction

This part of the review deals with analytical techniques that have been applied to the determination of thiosalts in various media. Classical laboratory chemical techniques such as titration, gravimetric analysis and colorimetric techniques as well as instrumental methods that have been applied to thiosalt analysis are covered. Performance of these techniques in terms of sensitivity, selectivity, reproducibility and robustness is examined, and medical, environmental, industrial and mining applications are presented. Attention is also paid to sampling techniques used in these applications. Finally, emerging analytical techniques, which hold promise for thiosalt analysis, are highlighted.

2.2 Methods of chemical analysis of thiosalts

Analytical methods are available for the determination of thiosalt species both collectively as total thiosalts and as the individual species: thiosulfate, trithionate, tetrathionate, pentathionate and hexathionate (Miura et al., 2001; Takano and Watanuki, 1988; Miura et al. 1986). When these species are in a mixture it is apparent that the chemistry will be more complicated than when they occur as individual species. Thus to obtain a measure of the thiosalt speciation in a given reservoir, the sampling protocols must ensure a representative unbiased distribution of samples and preserve speciation. When this approach is combined with analysis that can quickly provide reliable data on the concentration of each species under specific conditions, then a method can be considered to give truly representative analytical results. Below we discuss sampling methods and various analytical methods which have been applied to different situations and conditions for determining individual species as well as more complicated mixtures of thiosalts.

2.2.1 Wet Chemistry Techniques

2.2.1.1 Titrimetric Methods

Titrimetric methods have been applied to the determination of thiosulfate, sulfite and sulfide due to the accurate stoichiometry of the reaction between these species and the titrant that in many cases is iodine (I_2) or iodate. In addition, oxidizing agents such as permanganate or bromate may also be used in the determination of thiosulfate concentrations in samples. Although the classical titration technique is not very sensitive, potentiometric methods have been reliably used for most determinations (Ciesielski et al. 2001).

Thiosulfate has been determined with other sulfur species, particularly sulfide and sulphite, using formaldehyde to mask the sulfite by forming a stable formaldehyde-bisulphite complex and titrating the excess iodine with standard thiosulfate solution as shown below (Harris, 2010):

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^- \quad (11)$$

$$HSO_3^{2-} + I_2 + H_2O \rightarrow SO_4^{2-} + 2I^- + 3H^+ \quad (12)$$

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 2I^- + 3H_2O \quad (13)$$

$$Na_2SO_3 + HCHO + H_2O \rightarrow CH_3(OH)\,SO_3Na + NaOH \quad (14)$$

A blank titration is performed to determine the equivalence of iodine consumed by the thiosulfate and also to determine the equivalence of sulfite present.

2.2.2 Instrumental Methods of Analysis

Several analytical methods have been developed to overcome the low sensitivity and selectivity of the conventional methods. Thesemethods have found applications in almost all areas of research, industry and government for mining-related applications; wet chemistry related techniques and instrumental analysis of thiosalts complement one another for specific applications.

2.2.3 Chromatographic analysis

2.2.3.1 Ion chromatography (IC) and liquid chromatography (LC)

IC is a reliable and proven technique for the analysis of inorganic ions in environmental as well as other media. The technique makes use of columns packed with either anion or cation exchange resins with spectrophotometric, conductivity or electrochemical detectors. Several variations of the technique also exist (Jeffrey and Brunt 2007; Miura et al. 1998).

Analysis of sulfur species has focused on sulfate but awareness of the environmental impact of the intermediate sulfur species, particularly the thiosalts,have led to the development of IC techniques for their analysis. Friedhelm et al. (1993) developed an IC technique for the determination of tetrathionate and thiosulfate species in natural samples and microbial cultures. In this work, separation was achieved on a Sykam LCA A08 polymer-coated, silica based anion exchange column thermostated in a column oven and with UV detection at 216 nm. Samples were filtered with cellulose filters (0.45 μm) before analysis. The eluent used in this method was a mixture of acetonitrile and methanol. The method was further used to analyze sulfur species in soil as well as sediment samples. Detection limits were, however, in the lower nanomolar range. Interferences were however pronounced where eluents came into contact with metallic components and passed through the plastic solvent delivery system.

Takano et. al (1988) reported a pioneering work in liquid chromatographic separation and polarographic determination of aqueous polythionates and thiosulfate. In this work, a simple and moderately sensitive method was developed and used to separate a mixture of polythionates on a HPLC column with electrochemical detection. Separation was achieved on an anion exchange column with isocratic citrate buffer, and confirmed with a UV detector. However electrochemical detection was a challenge since the half-waves of the polythionates are similar and overlap. Further separation of the half-waves was achieved by various salt-alcohol mixtures to enable better separation and

simultaneous determination of the polythionates for which ethanol-CsCl-TMC mixture proved to be the best supporting electrolyte for optimum separation of the half-waves. The presence of high concentrations of pentathionate, however, lead to further overlap of half-waves and a second supporting electrolyte had to be used to achieve the best results.

Miura et. al. (2001) demonstrated the separation and detection of thiosalt species by postcolumn reduction of iodine with azide after reaction with the separated species on an octadecylsilica (ODS) column and elution with acetonitrile-water mobile phase. Tetrapropylammonium salt was used as an ion-pair agent in the separation. Iodine was detected as triiodidespectrophotometrically at 350 nm catalysed by each thiosalt species after separation in the column. Figure 9 shows the resolution of the method on a TSK ODS-Ts column and applied to a diluted sample of hot-spring water.

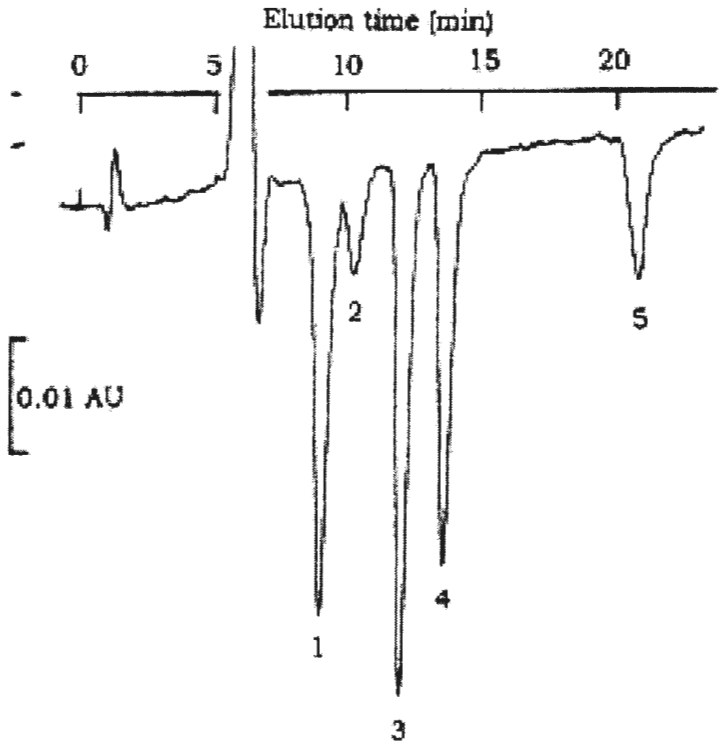


Figure 9 Chromatogram of diluted hot spring water (Miura et al, 2001) 1: $S_2O_3^{2-}$,2: $S_3O_6^{2-}$, 3: $S_4O_6^{2-}$, 4: $S_5O_6^{2-}$, 5: $S_6O_6^{2-}$

2.2.3.2 Spectroscopic analysis (IR, UV)

Several spectroscopic analyses have been used for the analysis of thiosalt species, either as single species or as a mixture of thiosalts. Methods which have been applied include infrared (IR)and ultra-violet (UV). For instance Muira and Koh (1986) showed that pentathionate can be oxidisedstoichiometrically via reaction with permanganate in a similar fashion as the reaction of thiocyanate with permanganate in an acidic medium. The measurement is indirect as the amount of iodine formed (as triiodide) after an excess of permanganate has been used for the reaction is measured on a Shimadzu Model UV-240 recording spectrophotometer with a 10-mm quartz cell and temperature regulator.

Koh and Muira (1987) performed another spectrophotometric determination of sulfide, sulphite and thiosulfate in a mixture by measuring the absorbance due first to thiosulfate, sulfide and sulfite and then masking sulfite with formaldehyde and determining thiosulfate and sulfide. They finally measured thiosulfate alone. Attempts were also made to determine the stabilities of sulfide and sulphite in their mixtures. The procedure of sulfide removal in order to be able to achieve accurate measurement of thiosulfate involved the precipitation of sulfide with zinc carbonate hydroxide and filtering. Interferences from ions such as Cu (II) and Fe (III) as well as Mn (II) could not be totally eliminated.

This method was successfully applied in the determination of sulfide, sulphite and thiosulfate in several fumarolic condensate solutions. Table 3 shows a summary of one such determination.

Table 3. Determination of sulfide, sulphite and thiosulfate in fumarolic concentrates

Sample	S^{2-} (µmol)	SO_3^{2-} (µmol)	$S_2O_3^{2-}$(µmol)
A	7.12	314	1.96
B	Not detected	0.06	0.36
C	0.07	0.12	0.52
D	7.58	44.1	0.64

In another study, tetrathionate was reacted with iodate and the iodide formed was measured spectrophotometrically as triiodide (Miura et al. 1991). Tetrathionate was quantitatively oxidised in an acidified medium with standard iodate solution to sulfate according to the equation:

$$3S_4O_6^{2-} + 7IO_3^- + 9H_2O \rightarrow 12SO_4^{2-} + 7I^- + 18H^+ \quad (15)$$

Iodate-free blanks were prepared and measured to correct for the errors in the absorbances. However interferences from other ions present such as Cu (II), iron (II) and nitrite pose serious errors in the procedure even when they are present in small quantities.

This procedure is similar to the previous discussion and indicates the difficulty in the determination of individual thiosalts in the presence of the others using spectrophotometry because of their similar physical and chemical properties (Faou et. al., 1990).

Other spectrophotometric studies of thiosalts have been done in addition to the above.These techniques all have the underlying requirement of masking and derivatizing in order to determine the quantity of each thiosalt species present. Thus, no one method has been applied to simultaneously measure all the thiosalt species, and most of the methods have been used when derivatization or conversion of one form of the compound to another is a requirement in order to achieve meaningful results. For example methods such as sulfidolysis (Koh et. al. 1988) and cyanolysis (Lieske et. al.,

1996) have been used to convert between thiosalt species or to another sulfur compound and detected. However propagation of errors without the proper calibration and standardization technique is inevitable.

2.2.4 Electrophoretic analysis (CE)

Extensive capillary electrophoretic workhas been done on sulfur oxyanions species in different media. This powerful analytical technique involves the separation of the analytes in an electrolyte medium with the application of a strong electric field and detection by spectrometry (absorption, fluorescence, thermal lens, Raman, chemiluminescence, mass spectrometry) or electrochemically (conductivity, potentiometry, amperometry) .

This technique has advantages over the most used analytical technique for anions, that is, ion chromatography as it is fast, uses cheap consumables, has high separation efficiencies, and is tolerable to different sample matrices. In addition it has very high sensitivities compared to other methods such as the IC and it can be coupled to mass spectrometry detectors. Thus it serves as an attractive complement to IC.

In addition, several electrolyte systems are available and have been applied to the separation of anions in addition to individual as well as mixtures of thiosalt species in different environmental media such as ground and surface water, waste water, plant and food materials, forensic media and industrial processes (W. Buchberger et. al., 1992, Corr et. al., 1996, Harrold et. al., 1993, Jones et. al., 1992, Rhemrev-Boom et. al., 1994, Zemann 1997, Kuban 1997). However only a few publications have focused on thiosalt species specifically.

One classic CE method (Motellier and Descostes, 2001) was the application of an indirect CE method to monitor sulfide (H_2S/HS^-), thiosulfate ($S_2O_3^{2-}$), tetrathionate ($S_3O_6^{2-}$), trithionate ($S_3O_6^{2-}$), sulphite (HSO_3^{2-}/SO_3^{2-}), sulfate (SO_4^{2}), and peroxodisulfate ($S_2O_8^{2-}$) in aqueous medium. In this method the optimized electrolyte

composition was sulfosalicylic acid (2 mM) as chromophoric probe, water osmotic flow modifier OFM-OH (0.5 mM) to control the electro-osmotic flow in the capillary and Bis–Tris as buffer to maintain a pH of 7.

The method showed a linear calibration curve for all species under consideration with LODs in the low µM to mid µM range. The method, however, did not give a direct measurement of the thiosalt species. Sulfate ion gave a single peak whereas the other species gave multiple peaks indicating impurities in the sample or other side reactions. The trithionate peak was derived from the sulfitolysis process so it was not directly detected. This method therefore needs to be optimized for direct detection of the analytes. An electropherogram obtained from the experiment is shown in Figure 10:

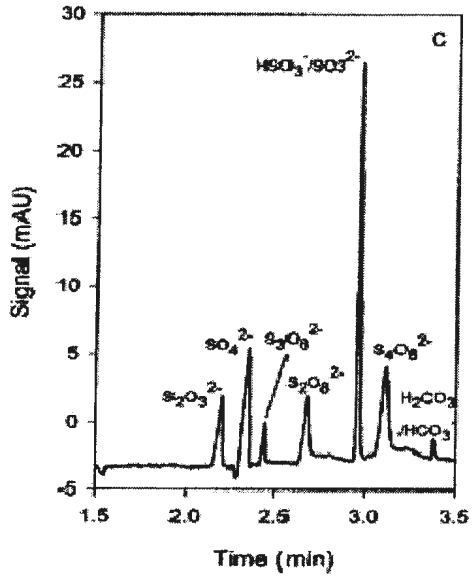


Figure 10 Electropherogram of sulfur species: 2 mM SULSAL-0.5 mM OFM-OH electrolyte system, pH 7.00, voltage -25 kV and indirect detection at 214 nm (Motellier and Descostes, 2001)

Daunoravicius et al.(2002) utilized aiodimetric titration for the detection of sulfides to perform an in-capillary derivatization of the thiosalt species and detection with UV-Vis

detection. In this experiment thiosulfate, sulfide and sulfite were separated by capillary electrophoresis and detected by reaction with iodine injected from the anodic end of the capillary. The iodide ion formed after the reaction under the counter electroosmotic conditions. The principle of the method is shown in Figure 11:

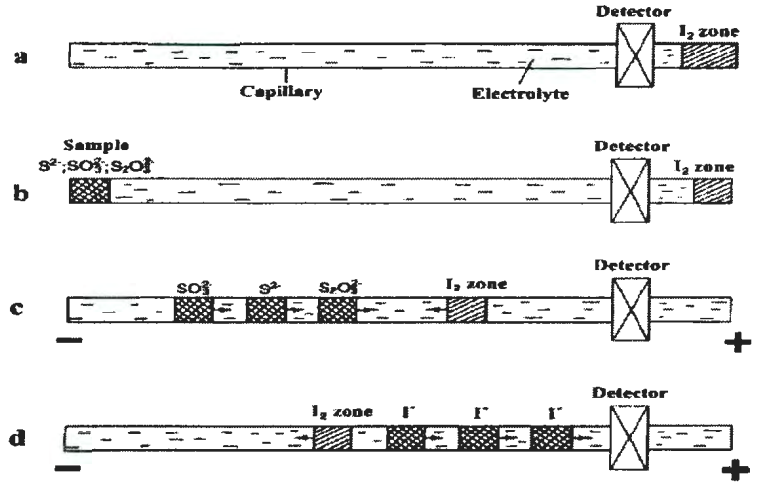


Figure 11 Principle of in-column derivatization of thiosulfate, sulfide and sulphite with iodine (Padarauskas, 2002)

First, the iodine is injected at the anodic end of the capillary followed by sample injection at the cathodic end. Application of high voltage results in the separation of the sulfur species, reaction at the iodine zone and migration of the formed iodide towards the detector.

The method was further applied to the determination of sulfur species in a diluted sample of spent fixing solutions generated during the electrolytic oxidation process. Electropherograms obtained from the experiment (Figure 12) show a fast analysis time with baseline separation of all analytes in less than 4 min.

This method has not, however, been applied to determine the other thiosalt species and indirect measurements may not give the most accurate results compared to direct determination. Statistical differences between direct and indirect method were small of

the analysis and further improvements could be developed with both internal and external calibrations.

Padarauskaset. al. (2000) developed and applied a method of anodic-oxidization and determination of the oxidation products of thiosulfate by CE. Species detected by this method include thiosulfate, tetrathionate, pentathionate and hexathionate. Both indirect and direct methods of detection of the analytes were applied in this determination. Trithionate was not detected either because it is not present or because the method was incapable of detecting it. In addition, the detection sensitivity for tetrathionate was poor and further optimization is necessary.

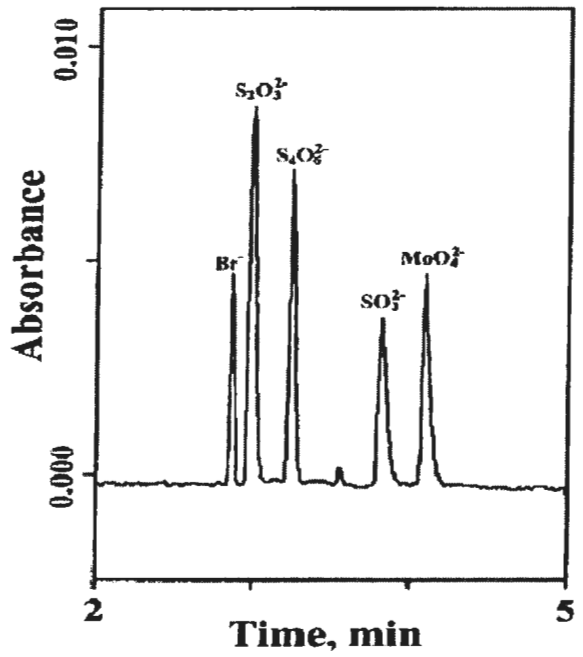


Figure 12 Electropherogram of diluted sample (1:500) spent fixing solution Conditions: Background electrolyte: 20 mMTris-chloride, pH 8.5; I2 : 1 mM; Injection: I2 injected at 20 psi, 0.01 min; sample injected at 0.5 psi, 8 s; applied voltage -30 kV; detection at UV wavelength 214 nm

Several other publications on CE separation of sulfur-containing compounds (not particularly on only thiosalts but other sulfur species) have been made which could be applied in thiosalt analysis as well. In addition, new and powerful CE techniques and electrolyte systems continue to be developed and thus prove to hold great future for separation, detection and quantification of thiosalt species.

2.2.5 Gravimetry and Thermal analysis (calorimetric, DTA, Microthermal, TGA)

Gravimetric methods have been used traditionally for analyzing precipitated ions in solution. The idea is that the analyzed precipitated form should be insoluble, pure and of known composition to enhance quantification. Most ions, including sulfate (SO_4^{2-}) have been analyzed by precipitation and gravimetric methods. Sulfate is precipitated usually in the form of barium sulfate ($BaSO_4$) but interferences occur from other ions present in the solution such as NO_3^-, Pb^{2+}, Fe^{3+} and Ca^{2+} making analysis somewhat challenging. (Harris, 2010).Gravimetry is also used to determine the purity of salts such as those of tetrathionate and trithionate for further analysis.

Few thermal analytical methods exist for the analysis of thiosalt species. In most studies only one or two of the thiosalt species are used in the analysis and thus, the trend in the behavior of the thiosalt species are difficult to correlate. In one study (Piękoś et. al., 2001) thiosulfate was partially decomposed by orthosilicic acid and the products by differential thermal analysis (DTA) and thermal gravimetric analysis (TGA).

$$S_2O_3^{2-} + 2H^+ \rightarrow [H_2S_2O_3] \rightarrow S + SO_2 + H_2O \qquad (16)$$

The method was used to analyze complex systems consisting of hydrated silica, sodium thiosulfate and elemental sulfur. The DTA, DTG and TG in Figure 13 below show the decomposition pattern of the degradation of the anhydrous salt followed by air-oxidation of the released sulfur.

The thermal analysis allows for identification of species undergoing oxidation and other thermal changes.

$Na_2S_2O_3^{2-} \rightarrow Na_2SO_3 + S$ (17)

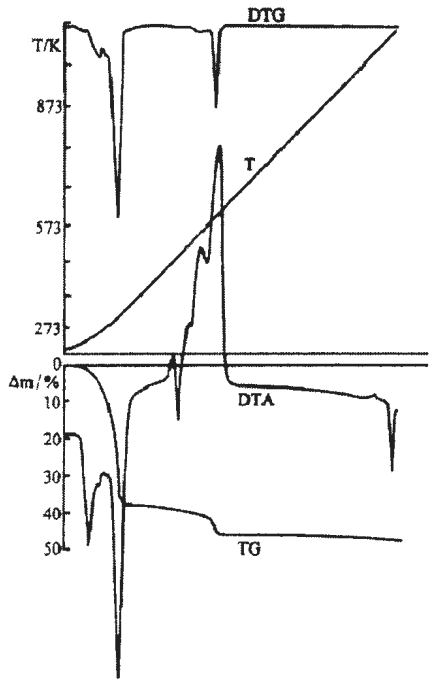


Figure 13 DTA, DTG and TG curves of thermal decomposition of sodium thiosulfate hydrate. (Figure used with permission)

2.2.6 Electroanalytical techniques

Several electroanalytical techniques have been applied for determination and quantification of thiosalts in various media. An in-situ nitrate ion-selective electrode (ISE) method was developed by Yoshiko et. al. (2008) to analysepolythionates in a crater lake. In this method a laboratory sample solution containing polythionates was set at conditions existing in the crater lake, stirred with a DC magnetic stirrer and electrode potentials measured with a pH/mV temperature meter after calibration of the ISE meter. All polythionates were detected except trithionate because of its instability in acid medium. Monitoring of the polythionates indicated that just before eruptions concentrations fall far below analytical limit of detection due to decomposition shown by the equation:

$S_{x+1}O_6^{2-} + HSO_3^- \rightarrow S_xO_6^{2-} + S_2O_3^{2-} + H^+$, where $n \geq 3$ (18)

Reproducibility was a challenge at polythionate concentrations below 10^{-2}mM but the method was selective, reproducible and convenient for monitoring polythionates in the concentration range of 10^{-3} M to 10^{-1} M. In addition, the method could only account for total polythionates and not the individual thiosalt species.

The method showed good agreement with a microboreHPLC column technique developed by Takano etal. (1984) for polythionates using a mobile phase of 0.1 M $KHPO_4$ solution (pH 3.5) with acetonitrile (ACN) solution 25 v/v %.

Irena et al. (1997) performed electro-analytical experiments to determine concentrations of thiosulfate and sulfide species in aqueous environments based on the interactions between the sulfur species and the mercury electrode used in the experiment. Sulfur species are known to have specific interactions and sensitivities towards electrochemical methods. The method was applied to marine samples from anoxic environments to determine sulfur speciation and concentrations. A linear sweep voltammetry (LSV) of the mixture in an electrolyte medium of 0.5 M NaCl and 3 x 10^{-3} M $NaHCO_3$ was performed for the analysis. The different voltammetric peak responses of $S_2O_3^{2-}$ and S^{2-} at different applied potentials were used for the characterization after calibration with standard solutions.

Direct measurement using the above method for thiosulfate determination requires acidification and purging of the solution of sulfide before measurement in addition to the adjustment of the solution pH to 8.3 similar to conditions in the natural aquatic system. Thiosulfate displays a voltammetric peak at about -0.15 V whereas the other species display peaks between -0.6 V and -0.7 V.However concentration of S^{2-} must be below 5 x 10^{-5} M to enable accurate measurements of $S_2O_3^{2-}$ and reduce interference.

2.3Validation and application of analytical techniques

Validation of analytical techniques is necessary in order to achieve reliable results as well as to be able to compare the method developed or applied to other existing techniques. This is to make the method acceptable for use. The method has to respond to an intended purpose in terms of its 'method specificity, linearity, accuracy, precision, range, limit of detection, limit of quantification and robustness' (Harris, 2010).

Breaux et al. (2003) indicated that a well-developed analytical technique must have the ability to be validated easily. The challenge, however, has been the reproducibility and repeatability of most methods where several individual scientists and different laboratories obtain results with large variations.

Several authors have also emphasized the need for improvement of existing and new analytical techniques and validation to meet guidelines such as the IUPAC/ISO/AOAC International Harmonization Protocols on Collaborative Studies (Horwitz et. al., 1988, 1995, IUPAC).

It is essential that methods also are assessed in collaboration with other scientists and laboratories a they are developed. This is particularly important for thiosalt analysis as methods of analysis need to ensure robust industrial application in order to meet obligations of monitoring and regulation as well as for universal acceptance.

2.4 Applications of analytical techniques to real samples

Several analytical methods have been applied to the determination of sulfur compounds in environmental media including surface water, soil and in mine waste. Analytical techniques have drawbacks depending on the required selectivity and sensitivity required for the analysis. Matrix effects and interference in analysis are very important to consider in any analysis. Methods discussed above all have their sensitivities, dynamic range for analysis and advantages.

In a study to separate gold thiosulfate leach solutions using capillary electrophoresis (O'Reilly et al., 2003) complex formation of gold thiosulfate, reactions between the sulfur oxy-anions as well as high ionic strength of samples were issues which needed to be addressed in order to obtain reliable analytical results. Capillary electrophoretic analysis also requires low concentrations of samples in order to get a good dynamic range for quantification of analyte concentrations. Thus real samples need to be diluted in order to obtain an acceptable ionic strength of samples as well as linear dynamic range for quantification.

Ion chromatographic analysis of some sulfur containing ions also has its drawbacks although it is a well-established and validated tool for inorganic ion analysis particularly anions (Haddad et al., 1999). In one study involving oil shale retort by-product water ion chromatographic studies reported good separation and detection of sulfur containing anions in the water (Poulson and Borg, 1987). However quantification was difficult as most of these ions are unstable and derivation is necessary in order to achieve reliable results.

2.5 Sampling Techniques for thiosalts

Sampling from mine tailings presents a challenge to the analyst since conditions and detailed information about the treatment process as well as the structure of the pond is necessary. Depending on the analytical method, sample preparation and management may vary, but a well-defined strategy is necessary to maintain sample integrity. As such it is important to have a good knowledge of the geochemical characteristics of the environment in which the thiosalt species occur to be able to access the samples and reduce error in analysis. Appropriate storage conditions are also an indispensable part of good sampling procedures and necessary for preserving the speciation of sulfur species in the sample. Thiosalt species can show different speciation if the sample is exposed to oxidizing environments or during sample preparation procedures. Therefore it is important to understand the effects of such procedures and take precautions during sampling.

In one study ion-exchange techniques were used to sample and preserve thiosalts species from the Yellowstone National Park in Wyoming, USA (Druschel et. al., 2003c). In this procedure, thiosalts from a hydrothermal solution were sequestered on resin. The researchers compared the performance of two types of anion exchange AG resins (Bio-Rad AG1-X8 AND AG2-X8) with different affinities toward the different sulfur oxyanions for use in the sampling. Elution after loading the samples on the column was done using different concentrations of KCl. Analysis of the eluted samples was achieved with a Dionex DX-500 ion chromatography system equipped with an electrochemical detector using an isocratic elution with a concentrated sodium bicarbonate/sodium carbonate eluent solution. Recoveries ranged from 87% to 100% for the prepared concentrations of the sulfur species. Table 4 below summarizes the selectivity of the resins used in this study.

Table 4. Relevant selectivities of anion exchange resins used in study

	Selectivity with respect to OH^-	
Ion	AG1-X8	AG2-X8
Cl^-	22	2.3
SO_4^{2-}, HSO_4^-	85	15
$S_2O_3^{2-}$	~275	~90
$S_xO_6^{2-}$ (x>2)	Fully retained	~500

A variety of changes including oxidation (driven by exposure to oxygen in air) and reaction with other thiosalt species can occur, it important to be able to preserve the thiosalt sample once collected. One way is to fast-freeze the samples if laboratory analysis is not immediately done or on-site analysis kit is not available (Kuyucak et. al. 2001). Fast-freezing can be done by immersing small volumes of samples in liquid nitrogen or in a mixture of dry ice and acetone or ethanol. Sizes of samples taken from the sampling points can range from 1 mL to 1 L depending on the method of preservation and the type of analysis required. Typical sample sizes have ranged from 5 mL to 60 mL (Druschel et. al., 2003c) and even to 1 L (S´liwka-Kaszyńska et al. 2003).

Keeping the samples frozen ensures that changes to the sample are minimal and analysis can be trusted.

Studies done on the effect of freezing and thawing on some thiosalt species and consequently on their stability at different pH ranges show differences in the concentrations of the species before and after freezing (Vongporm, 2008). The differences are higher in those species subjected to slow freezing (normal freezing) than in those subjected to fast freezing in liquid nitrogen. Difference for fast freezing samples areup to ±10%. However; thiosalt species buffered at pH between 4 and 7 show the smallest variation in concentration difference. The experiment shows that some thiosalt species such as trithionate are more reactive than tetrathionate or thiosulfate at room temperature and even can be seen to react at 4 ^{o}C. Therefore, sampling thiosalts and further storage presents a challenge and precautions need to be taken to ensure that species present at sampling do not change during analysis as this would present faulty results.

Since oxidation of thiosalts continues in the mine tailing waters until all the thiosalts are converted into the end product, which is sulfate (SO_4^{2-}) under aerobic conditions, (Druschel et al., 2003; Schppers et al., 1999) it is important also that continuous monitoring is done. In addition, consistent application of sampling protocol is important in ensuring that sample integrity is maintained and that interference from contaminants are reduced or easily masked. Several water sampling protocols exist in both governmental and private monitoring even though few exist for specifically thiosalts in tailings. However the principleremains essentially similar. Information generally required from field sampling of thiosalts in tailing ponds would include but not limited to details of sampling site map with coordinates (e.g., GPS points), sampling points, date and time of sampling, climatic conditions such the weather, temperature, condition of surface water, sample pre-treatment and storage, among other information. Knowledge of the geochemical nature of the mine or tailing site would also enhance the quality of the sampling protocol. Several sampling models as well as simulations also exist for ensuring representative sampling (Debba et al., 2009).

3. Kinetic and Equilibrium Studies for major species

The following section reviews the information related to thermodynamics and kinetics studies present in the literature.

There have been several studies related to reaction kinetics involving polythionates. However; most of these were carried out under different conditions that make direct comparison difficult. These studies identify temperature, pH and reagents as key players in the reactions of thiosalts. The next section gives a brief summary of the pertinent studies grouped on the basis of type of thiosalt.

3.1 Thiosalt Thermodynamic and Equilibrium Information

Any given system will be at equilibrium when a minimum Gibbs free energy level is reached. Thermodynamic equilibrium can be used as a tool in kinetic analysis and product speciation.

The standard Gibbs free energy is related to the equilibrium constant with the following equation

$$\Delta G^o = -RTln(K_{eq}) \qquad (19)$$

In the case of thiosulfate, Thauer et al. (1977) reported values of free Gibbs energy for reactions involving this compound at standard conditions (25°C and pH=7 set by adjusting H^+ concentration). Table 5 shows the reactions and values reported by Thauer et al. (1977).

Table 5 Reactions and Gibbs free energy information for thiosulfate degradation

Reactions involving thiosulfate as reactant	ΔG° (kJ/mol)	Reaction involving thiosulfate as product	ΔG° (kJ/mol)
$S_2O_3^{2-} + 4H_2 \rightarrow 2HS^- + 3H_2O$	-174.1	$S_4O_6^{2-} + H_2 \rightarrow S_2O_3^{2-} + 2H^+$	-84.5
$S_2O_3^{2-} + 2H^+ + 2H_2 \rightarrow 2S + 3H_2O$	-118.4		
$S_2O_3^{2-} + H_2 \rightarrow HS^- + SO_3^{2-} + 2H^+$	-1.1		

Table 6 outlines Gibbs free energy of formation under standard conditions of thiosalt species and other related compounds (Thauer et al., 1977).

Table 6 Thermodynamic information for thiosalts

Substance	State	ΔG_f° (kJ/mol)
HS^-	Aqueous	-12.05
SO_3^-	Aqueous	486.6
SO_4^{2-}	Aqueous	744.63
$S_2O_3^{2-}$	Aqueous	513.4
$S_3O_6^{2-}$	Aqueous	958.1
$S_4O_6^{2-}$	Aqueous	1022.2

This information is used to determine the equilibrium concentrations of thiosalts; reaction products are a function of temperature and pH through minimization of Free Gibbs energy as Vongporm (2008) showed by an equilibrium analysis using HSC software:

$$\Delta_r G^o = \sum \Delta_f G^o(Products) - \sum \Delta_f G^o(Reactants) \quad (20)$$

In the case of trithionate, the thermodynamic information available is presented in Table 7 modified from Thauer et al. (1977) at standard conditions and pH=7:

Table 7 Reactions and Gibbs free energy information for trithionate degradation

Reactions involving trithonate as reactant	ΔG° (kJ/mol)	Reaction involving trithionate as product	ΔG° (kJ/mol)
$S_3O_6^{2-} + H_2 \rightarrow S_2O_3^{2-} + SO_3^{2-} + 2H^+$	-121.8	$3SO_3^{2-} + 4H^+ + H_2 \rightarrow S_3O_6^{2-} + 3H_2O$	-50.2

Finally, tetrathionate participates in various reactions as reactant or product. The thermodynamic information as reported by Thauer et al. (1977) is presented in Table 8:

Table 8 Reactions and Gibbs free energy information for tetrathionate degradation

Reactions involving tetrathionate as reactant	ΔG° (kJ/mol)	Reaction involving tetrathionate as product	ΔG° (kJ/mol)
$S_4O_6^{2-} + H_2 \rightarrow S_2O_3^{2-} + 2H^+$	-84.5	none	

Unlike the other compounds, there is no experimental data reported for tetrathionate as a product of the oxidation despite the fact that it is the most common product of thiosulfate degradation.

3.2 Thiosulfate Reactions

3.2.1 Temperature and pH as only variables

Thiosulfate is usually stable in neutral and alkaline environments; however, in alkaline media at high temperatures (i.e., above 70°C) thiosulfate decomposes to sulfate (SO_4^{-2}). In acidic media it is very reactive and oxidizes to tetrathionate ($S_4O_6^{2-}$) in the presence of oxidants such as oxygen (Xu and Schoonen, 1995; Rabin, 1998).

Mizoguchi et al. (1976) proposed the following pathways for reactions of thiosulfate in acid media shown in Figure 14.

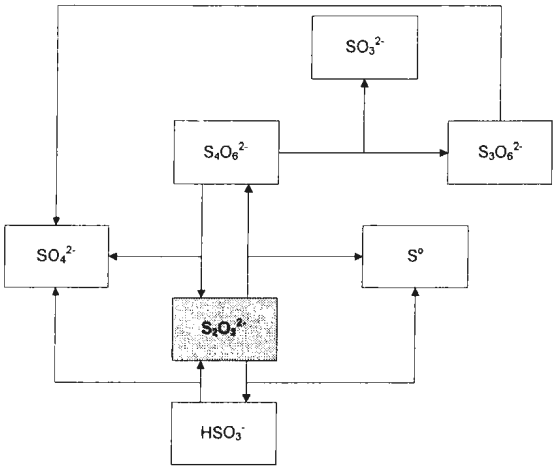


Figure 14 Thiosulfate reaction pathways (modified from Mizoguchi et al., 1976).

Wasserlauf and Dutrizac (1982) reported the conversion of thiosulfate to tetrathionate, as shown in reaction 21, under neutral to mildly acidic conditions.

$$2S_2O_3^{2-} + 2H^+ + \tfrac{1}{2}\, O_2 \rightarrow S_4O_6^{2-} + H_2O \qquad (21)$$

In this case, the protons act to catalyze the reaction. Suzuki (1999) also identified tetrathionate as the main product of thiosulfate dissociation in acid media. Xu and Schoonen (1995) proposed decomposition of thiosulfate at 25°C, pH=2.9 and after 10 hours as shown in reaction 22. In this study, the authors noted that tetrathionate generated in reaction 21 could further react with O_2 yielding different products.

$$2S_2O_3^{2-} + H^+ \rightarrow HSO_3^- + SO_3^{2-} + 2S^\circ \qquad (22)$$

Sulfite (SO_3^{2-}) generated through this reaction could either form SO_4^{2-} (Habashi, 1981; Moses and Herman, 1990) or thiosulfate (Chen and Morris, 1972). A probable pathway is the disproportionation of thiosulfate in anoxic environments as proposed by

Jorgensen (1990) with the following reaction, with a reaction time of around 200 minutes:

$$2S_2O_3^{2-} + H_2O \rightarrow HS^- + SO_4^{2-} + 2H^+ \quad (23)$$

Finally, Mizoguchi et al. (1976) studied thiosulfate reactions at pH below 2.3 and high temperatures between 70 and 150°C and at least 3 hours of reaction. The reactions proposed are as follows:

$$5S_2O_3^{2-} + 6H^+ \rightarrow 2S_4O_6^{2-} + 2S^o + 3H_2O \quad (24)$$

$$S_2O_3^{2-} + H^+ \rightarrow HSO_3^- + S^o \quad (25)$$

$$3S_2O_3^{2-} + 2H^+ \rightarrow 2SO_4^{2-} + 4S^o + H_2O \quad (26)$$

The oxidation of thiosulfate in alkaline media under atmospheric conditions is usually a slow process, which requires a strong oxidant. At 125°C under saturated oxygen conditions and after 2 hours of reaction, thiosulfate follows a first order decomposition reaction as proposed by Rolia and Chakrabarti (1982) in reaction 27:

$$S_2O_3^{2-} + 2O_2 + H_2O \rightarrow 2SO_4^- + 2H^+ \quad (27)$$

Table 9 shows a summary of the kinetic information published for thiosulfate and Figure 15 shows the graphic comparison of the differential equations presented in the table.

Table 9. Summary of reaction rates reported for thiosulfate at acidic and basic conditions

Author	Reaction Rate	Conditions		Comments
		pH	T (°C)	
Xu and Schoonen(	$\frac{-d[S_2O_3^{-2}]}{dt} = 0.66M^{-2}s^{-1}[S_2O_3^{-2}]^2$	2.9	25	Initial rate method used

1995)				Reaction (22)
Rolia and Chakrabarti (1982)	$\frac{-d[S_2O_3^{-2}]}{dt} = 1.48x10^{-3}s^{-1}[S_2O_3^{-2}]$	12	125	Saturated oxygen conditions. Reaction (27)

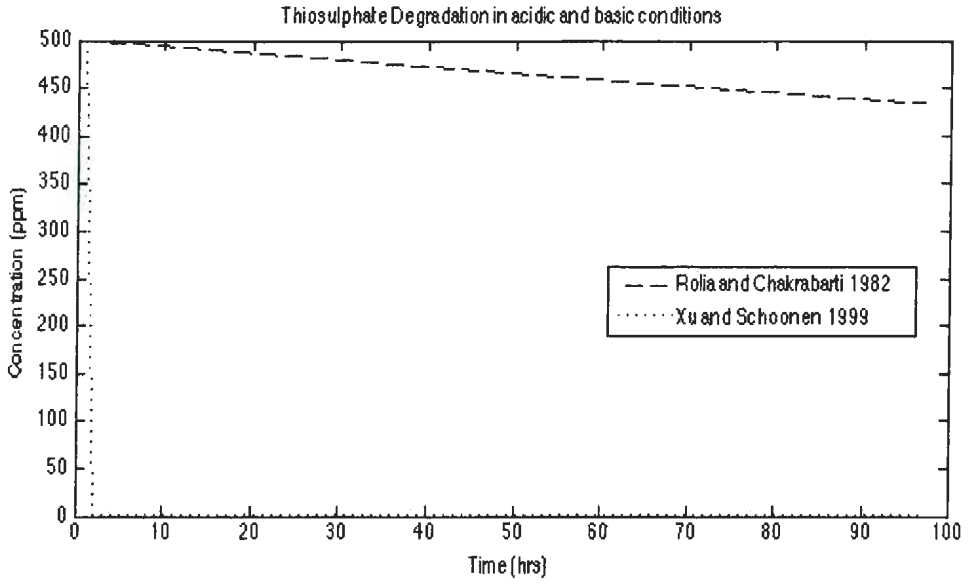


Figure 15 Degradation of thiosulfate in acidic and basic conditions as presented in Table 9.

3.2.2 Thiosulfate and Pyrite reactions

The role of catalysts in the oxidation of thiosulfate, and thiosalts in general, is extremely important in acceleration of the oxidation to sulfate. Pyrite (FeS_2), the most abundant sulfide (McLean, 1991), plays an important role in thiosulfate reactivity, enhancing the interaction of thiosalts with oxygen as a result of the electron configuration of the atoms in the exposed layers of the pyrite crystal structure (Druschel et al. 2004). Xu and Schoonen (1995) studied thiosulfate at pH=2.9 and temperature of 25°C under oxygen saturated conditions and anaerobic conditions. There was still thiosulfate reacting through disproportionation to sulphite under the anaerobic conditions. Pyrite has been identified as a precursor of thiosulfate in tailings ponds (Borda et al., 2004; Brimblecome, 2005; Garcia et al., 2005; Johnson, 2003; Xu and Schoonen, 1995),

especially at high pH where thiosulfate is stable (Rimstidt and Vaughan, 2003). The rate of formation of sulfate as a product of the reaction of thiosulfate in the presence of pyrite and oxygen proposed by Xu and Schoonen (1995) is:

$$R_{SO_4} = K[FeS_2][S_2O_3^-]^n \quad (28)$$

Where R is the rate of sulfate production at pH=2.9 and k is the calculated rate constant of $8.8\pm2.1\times10^{-7}$ moles sec^{-1} m^{-2} and a reaction order of 0.7. The pyrite term is express in terms of the surface area of the compound not concentration. An important observation in the Xu and Schoonen (1995) experiments is that the reaction rate drops, especially in neutral to basic pH. The proposed reaction of thiosulfate in the presence of pyrite is as follows (Xu and Schoonen, 1995):

$$S_2O_3^{2-} + 0.5O_2 + 2H^+ \rightarrow S_4O_6^{2-} + 2H_2O \quad (29)$$

Therefore, tetrathionate is expected to be the main product of the reaction of thiosulfate in the presence of pyrite at acidic conditions.

3.2.3 Thiosulfate and Iron (III) reactions

Similar to the reactions with pyrite, the presence of Fe^{3+} yields mainly tetrathionate as a product in low pH environments in studies that lasted 1 hour, according to the following reaction (Druschell et al., 2003a):

$$2S_2O_3^{2-} + 2Fe^{3+} \rightarrow 2FeS_2O_3^+ \rightarrow S_4O_6^{2-} + 2Fe^{2+} \quad (30)$$

Williamson and Rimstidt (1993) proposed that this reaction goes through a ferric thiosulfate complex intermediate as shown in reaction 28:

$$2S_2O_3^{2-} + 2Fe^{3+} = FeS_2O_3^+ \rightarrow S_4O_6^{2-} + 2Fe^{2+} \quad (31)$$

With the following reaction rate:

$$-\frac{d[FeS_2O_3^+]}{dt} = 10^{2.0\pm0.3}[FeS_2O_3^+]^{2\pm0.1} \quad (32)$$

This reaction that occurs for thiosulfate is several orders of magnitude faster than the degradation of tetrathionate (or trithionate) to sulfate under similar conditions; therefore the reaction rate of tetrathionate is considered to define the thiosalt oxidation process at pH between 2.65 and 3.09 and temperatures between 11°C to 33°C (Williamson and Rimstidt, 1993). Even though Druschell et al. (2003a) and Xu and Schoonen (1995) identified pyrite and Fe^{3+} as an important oxidant for thiosulfate, the same cannot be said for tetrathionate and trithionate. Druschell et al. (2003a) found that oxygen is a more efficient oxidant for tetrathionate than Fe^{3+}.

3.2.4 Thiosulfate and Cu (II) reactions

Another metal that has been studied as catalyst of thiosulfate reactions in the presence of oxygen is copper. Chanda and Rempel (1987) proposed the following pathways for thiosulfate oxidation to sulfate (Figure 16):

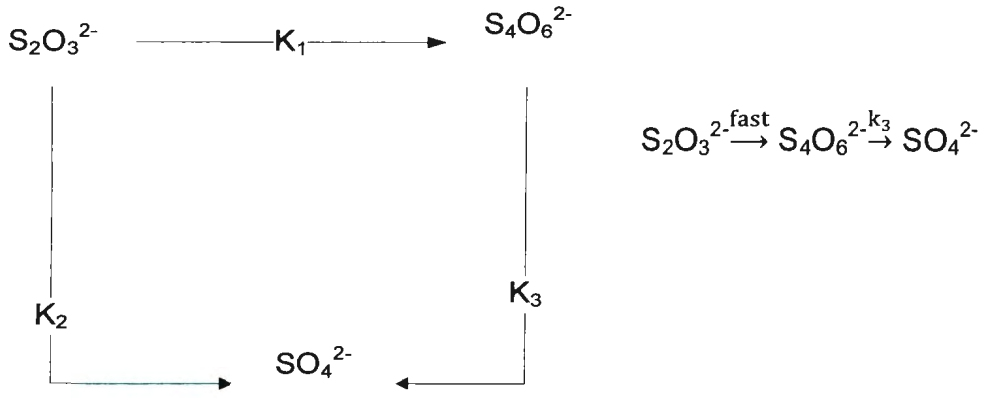


Figure 16 Reaction pathways of thiosulfateto sulfate in the presence of copper complexes.

Their study concluded that with low concentrations of thiosulfate(~5 mmol/l) and low pH, most of the thiosulfate will degrade to sulfate in the presence of copper. However, the reaction pathway goes through the formation of tetrathionate, which has a different reaction rate than for the oxidation of thiosulfate directly to sulfate hence, the reaction to sulfate is not complete at high concentrations of thiosulfate. They also suggested that the step between thiosulfate and tetrathionate does not involve oxygen, but that oxygen is necessary for the oxidation of tetrathionate. This is similar to the conclusions reached by Xu and Schoonen (1995) and Druschell et al. (2003a) in the presence of other catalysts. One key characteristic of these reactions are that they become significant at moderately high temperatures, ranging between 40 and 60°C. The reaction rate proposed by Chanda and Rempel (1987) for CuS/Cu_2S catalyzed air oxidation of thiosulfate is:

$$-\frac{d[S_2O_3^{-2}]}{dt} = (k_1 + k_2)[S_2O_3^{-2}] \quad (33)$$

The reaction is reported to be pseudo first order, where k_1 and k_2 depend on the temperature and CuS or Cu_2S presence according to Table 10:

Table 10 Rate constants for thiosulfate degradation in the presence of copper (modified from Chanda and Rempel, 1987)

Temp (°C)	Catalyst			
	CuS		Cu_2S	
	Rate Constant, k x 10^2 min^{-1}			
	k_1	k_2	k_1	k_2
40	2.36	0.4	2.99	0.95
50	5.1	0.86	5.01	1.8
60	11.34	2.04	9.1	3.7

3.2.5 Thiosulfate and Microorganisms

Common strains of S-oxidizing bacteria are *Acidithiobacillusferroxidans (A. ferroxidans)* and *Acidithiobacillusthiooxidans (A. thiooxidans)* which are airborne bacteria. Natural degradation will strongly depend on the available oxygen, nutrient concentrations, bacterial population, and temperature (Gould et al. 2004).In comparison, strains obtained from mining watersheds are acclimatized to more extreme conditions than bacteria growth in the lab. The microorganisms also play a role in the formation of thiosulfate or other polythionates from pyrite depending on conditions (Schippers et al. 1996b). Generally, the final product of microbial degradation of thiosulfate is sulfate with tetrathionate as a secondary product (Gould et al. 2004; Bernier and Warren, 2007, Wentzien et al., 1994), however, the generation of trithionate is also possible depending on the type of microorganism (Silver and Dinardo, 1981; Wentzien et al., 1994) according to the following general pathways:

$$\text{Thiosulfate} \xrightarrow[\text{enzyme}]{\text{Thiosulfate reducing}} \text{Sulfide} \rightarrow \text{Sulfate}$$

$$\text{Thiosulfate} \xrightarrow[\text{enzyme}]{\text{Thiosulfate oxidizing}} \rightarrow \text{Tetrathionate} \rightarrow \text{Sulfide or Trithionate}$$

The reaction time considered by Silver and Dinardo (1981) was around 144 hours. The reaction pathway will strongly depend on the microorganism present in the pond. For example, *Thiobacilusferroxidans* (*T. ferroxidans*) yield thiosulfate and tetrathionate; *T. tepidarius* yield dithionate and *T. versutus* oxidize thiosulfate without intermediates and accumulate sulfur (Wentzien et al., 1994). In some cases, the bacteria population will influence the final product of the reaction; however these final products will be also be determined by the conditions of the solution (Wetzien et al. 1994; Warren et al., 2008).

A key parameter for microbial degradation is pH. Silver and Dinardo (1981) established an optimal pH for *T. thioxidans* of 3.75 while Masau et al. (2001) reported an optimal pH of 5.0. Under acidic conditions, thiosalts will be susceptible to disproportionation, meaning that the compounds will oxidize regardless of the microbial activity. Warren et

al. (2008) identified disproportionation as important for the initial microbial processing of thiosulfate. At basic conditions, the most likely mechanism is that microorganisms change the oxidation state of sulfur oxidizing thiosulfate to tetrathionate and then to sulfate as reported in reaction 7 (Sorokin and Tourova, 2005).

Bernier and Warren (2007) study shows that *A. thiooxidans* reacts faster than A. ferroxidans and a combination of both microorganism with thiosulfate; also its reaction results in a lower pH of the solution. In addition, their study shows that the stable thiosalt species will depend on the bacteria present in solution. The sulfur species measured were thiosulfate, sulfate, elemental sulfur and tetrathionate. There was an overall deficit in total input of sulfur versus measured output of total sulfur, which could potentially indicate trithionate is present. The reaction pathways suggested by Bernier and Warren (2007) in a pH between 2 and 4 is similar to reaction 6.

The use of inhibitors such as metals, calcium carbonate, calcium fluoride and concrete (which main component is cement) can be used to control the thiosulfate reaction pathway by microorganisms (Schippers et al., 1996a; Silver and Dinardo, 1981). The inhibition effect of metals is not additive but it is directly related to their concentration (Silver and Dinardo, 1981).

3.2.6 Other thiosulfate reactions

Several authors (i.e. Horvath, 2008; Varga et al., 2006; Horvath and Nagypl, 1998; Read et al., 2001) have studied the oxidation of thiosulfate with different oxidants like iodate, chloride oxide, hypochlorous acid and potassium ferrate respectively.

In most of the studies, the final product is sulfate, sulfide or sulfite and in some cases tetrathionate appears as intermediate. The kinetics in these systems are complex and out of the scope of this paper.

3.3 Trithionate Reactions

3.3.1 Varying only Temperature and pH

Trithionate is stable in neutral and low pH environments; its reactivity increases with pH. The products of trithionate oxidation are thiosulfate and sulfate, but the extent and distribution depends on the conditions. Thiosulfate produced can also be subject to further reactions (Meyer and Ospina, 1982; Mizoguchi et al., 1976).

Meyer and Ospina (1982) followed the degradation of trithionate at pH between 3.5 and 4 and temperatures between 20 and 70°C; the reaction time depended on the temperature, in the case of the studies at 70°C the reaction reaches equilibrium around 10 hours. They reported an initial reaction forming tetrathionate and sulfate (reaction 29) and then to sulfate, sulfur dioxide and sulfur (reaction 30).

$$3S_3O_6^{2-} \rightarrow S_4O_6^{2-} + {}^1/_8S_8 + 2SO_4^{2-} + 2SO_2 \quad (34)$$

$$S_3O_6^{2-} \rightarrow {}^1/_8S_8 + SO_4^{2-} + SO_2 \quad (35)$$

For high temperatures, between 70 and 150°C, Mizoguchi et al. (1976) proposed the degradation of trithionate to thiosulfate and sulfate according to reaction 31. The reaction in this case reaches equilibrium at 1 hour:

$$S_3O_6^{2-} + H_2O \rightarrow S_2O_3^{2-} + SO_4^{2-} + 2H^+ \quad (36)$$

This same reaction is proposed by Wasserlauf and Dutrizac (1982) for the oxidation of trithionate pH below 7 and by Varga and Horvath (2007) in alkaline solutions around pH=12. As a result of the acidic conditions, thiosulfate produced in reaction 31 should undergo further oxidation to tetrathionate and sulfite (Mizoguchi et al., 1976). A summary of the kinetic information gathered by different authors is presented in Table 11 and the graphic comparison of the differential equations in Figure 17.

In Figure 17, it can be seen that the reaction rate is faster at higher temperatures as expected but the order of magnitude in the reaction constant is within the same order as well as the order of the reaction.

Table 11. Summary of reaction rates reported for trithionate at acidic conditions

Author	Reaction Rate	Conditions		Comments
		pH	T (°C)	
Ahern et al. (2006)	$-\frac{d[S_3O_6^{-2}]}{dt} = 1.2x10^{-2}\,h^{-1}[S_3O_6^{-2}]$	2	40	Initial rate method used
Miranda-Trevino et al. (2009)	$-\frac{d[S_3O_6^{-2}]}{dt} = 2.6x10^{-2}\,h^{-1}[S_3O_6^{-2}]$	2-4	4-15	Reaction (36)
Meyer and Ospina (1982)	$-\frac{d[S_3O_6^{-2}]}{dt} = 3.2x10^{-2}\,h^{-1}[S_3O_6^{-2}]$	3.5-4	35	Reaction (34, 35)

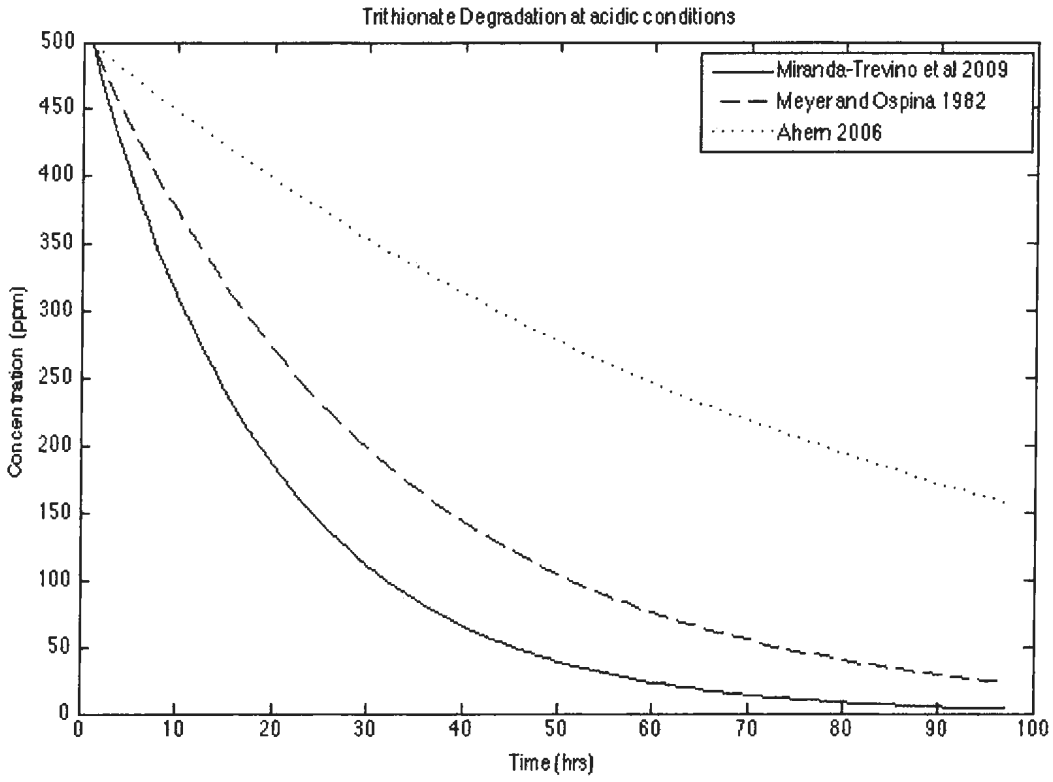


Figure 17 Degradation of trithionate in acidic conditions

Trithionate is more reactive in alkaline conditions. The proposed products of trithionate oxidation in basic solutions are the same as proposed for acid solutions in reaction 31 (Ahern et al., 2006; Rolia and Chakrabarti, 1982; Wasserlauf and Dutrizac,1982). However, Rolia and Chakrabarti (1982) noted that the reaction did not reach equilibrium during long runs as the thiosulfate generated continued to react to form sulfate. The kinetic information available under these conditions is presented in Table 12 and Figure 18.

Table 12.Summary of reaction rates reported for trithionate at basic conditions

Author	Reaction Rate	Conditions		Comments
		pH	T (°C)	
Rolia and	$-\frac{d[S_3O_6^{-2}]}{dt} = 4.1x10^{-3}\,h^{-1}[S_3O_6^{-2}]$	5.5-	80	Initial rate method used

Chakrabarti (1982)		12		Reaction (36)
Miranda-Trevino et al. (2009)	$-\frac{d[S_3O_6^{-2}]}{dt} = 1.9x10^{-3}\,h^{-1}[S_3O_6^{-2}]$	7-9	30	Reaction (36)

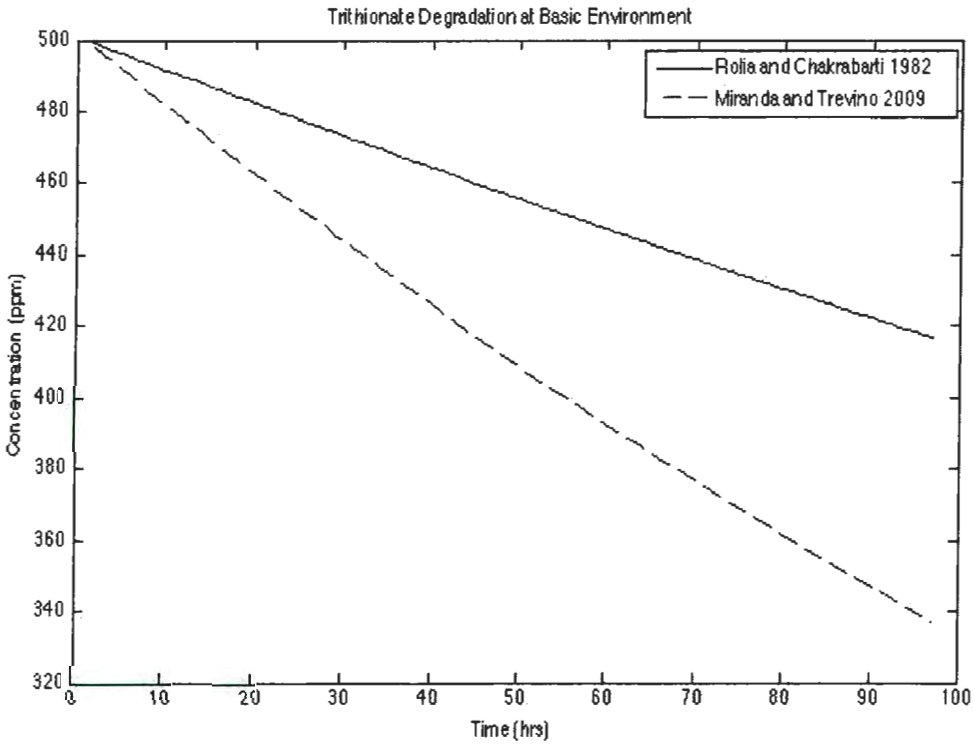


Figure 18 Degradation of trithionate in basic conditions.

3.3.2 Reactions in the presences of iron (III)

Depending on the conditions of the solution or the pond, trithionate can be catalyzed by different compounds. At low pH and in the presence of Fe^{3+}, trithionate oxidizes faster (equilibrium reached in 1 hour) than in the presence of oxygen alone according to the following reaction (Druschell et al., 2003a):

$$S_3O_6^{2-} + Fe^{3+}\ ½O_2 \rightarrow S_2O_3^{2-} + SO_4^{2-} + Fe^{2+} \qquad (37)$$

Druschell et al. (2003a) reported an initial reaction rate of $2x10^{-7}$ Ms^{-1} at a temperature of 35°C and pH of 1.5. Under these conditions, trithionate will react faster than tetrathionate. As presented in the previous section, thiosulfate in the presence of rich Fe^{3+} environments will degrade to either tetrathionate or trithionate and ultimately to sulfate.

3.3.3 Trithionate and Hydrogen Peroxide reactions

A common chemical used in the thiosalt treatment is hydrogen peroxide (Dinardo, 1998). However, Druschell et al. (2003b) found that there is little reactivity of trithionate with this compound; in fact in the synthesis of trithionate from thiosulfate hydrogen peroxide is a reagent (Kelly et al., 1994). The presence of hydroxyl radicals generated through the Fenton reaction (using Fe^{2+}/Fe^{3+} and peroxide) oxidized trithionate up to 14 orders of magnitude faster than peroxide alone (Druschell et al. (2003b).

3.3.4 Trithionate and Cu (II) reactions

In the presence of copper-sulfur complexes, trithionate is a reaction intermediate for the reaction of thiosulfate and tetrathionate to sulfate as proposed by Chanda and Rempel (1987), Figure 17. However under mildly acidic conditions, the reaction favours tetrathionate which reacts to produce sulfate without having trithionate as an intermediate. Although Chanda and Rempel (1987) did not include basic conditions in their experiments with copper complexes, they did identify trithionate as a product of tetrathionate under these conditions. However is not clear if copper complexes will catalyze trithionate as it is shown in Figure 19 above pH 7.

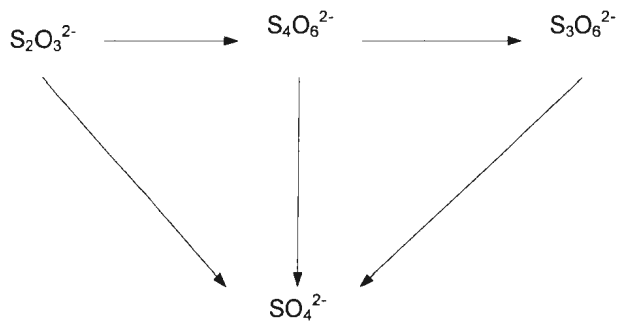


Figure 19 Thiosulfate reaction pathway in the presence of copper complexes (Chanda and Rempel, 1987)

3.3.5 Trithionate and microorganism reactions

As with thiosulfate, sulfur oxidizing bacteria (*Acidithiobacillusferroxidans*and *Acidithiobacillusthiooxidans*) accelerate trithionate degradation. Bernier and Warren (2007) followed thiosulfate and tetrathionate reactions using different strains and combinations of bacteria. They found that under certain conditions, up to 68% of the sulfur in the solution was not in the species measured. This could imply the formation of trithionate, which has a slower reaction in the presence of some bacteria under specific conditions. The former supports one of Silver and Dinardo (1981) proposed sulfide degradation pathways that identified trithionate as an intermediate:

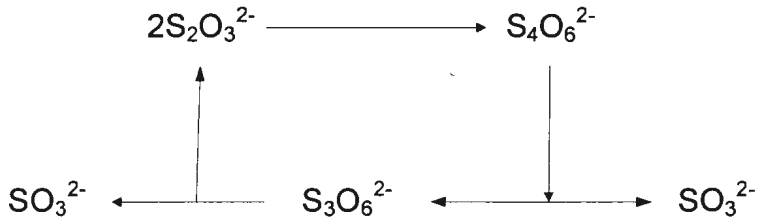


Figure 20 Sulfidedegrataion pathway proposed by Silver and Dinardo (1981)

Like most of the microorganisms, temperature and oxygen availability will strongly influence trithionate degradation (Gould et al., 2004).

3.3.6 Other trithionate reactions

Other authors have studied thiosalt reactivity under different conditions that are not directly related to mining processes. For example, Read et al. (2001) studied the reaction of thiosalts with potassium ferrate at 25°C. In the case of trithionate, the proposed reaction does not yield sulfate or sulfite but thiosulfate as follows:

$$6S_3O_6^{2-} + 10FeO_4^{2-} + 44H^+ \rightarrow 9S_2O_3^{2-} + 22H_2O + 10Fe^{3+} \quad (38)$$

The reaction is pseudo first order with a reaction rate constant of 2.9 $M^{-1}s^{-1}$ above pH 8.0; below that pH, the effect of the hydrogen ions yields intermediates that complicated the analysis. Read et al. (2001) followed the reaction for 48 hours.

3.4 Tetrathionate Reactions

3.4.1 Temperature and pH as only variables

Tetrathionate is highly stable in acid conditions. However, it degrades to thiosulfate and sulfate at pH near to neutral (Wasserlauf and Dutrizac, 1982). In an alkaline environment, tetrathionate degrades to thiosulfate and sulphite. There is limited information regarding the behaviour of tetrathionate in acid environments. Meyer and Ospina (1982) studied the reaction at pH 3.5 to 4 and temperature of 20 and 70°C proposing trithionate and pentathionate as the products of the reaction analyzed after 20 hours:

$$2S_4O_6^{2-} \rightarrow S_5O_6^{2-} + S_3O_6^{2-} \quad (39)$$

Their kinetic analysis indicates that tetrathionate oxidation is a second order reaction with a reaction constant at 20°C of 4.1 $M^{-1}hr^{-1}$.

In the presence of a strong alkaline media, tetrathionate oxidation will yield thiosulfate and sulphite according to reaction 35 in studies that lasted up to 40 hours (Varga and Horvath, 2007; Zhang and Dreisinger, 2002):

$$2S_4O_6^{2-} + 6OH^- \rightarrow 3S_2O_3^{2-} + 2SO_3^{2-} + 3H_2O \qquad (40)$$

Both authors reported trithionate as a probable intermediate in this reaction, similar to the reaction proposed by Rolia and Chakrabarti (1982) after 1 hour of reaction:

$$4S_4O_6^{2-} + 6OH^- \rightarrow 5S_2O_3^{2-} + 2S_3O_6^{2-} + 3H_2O \qquad (41)$$

Since thiosulfate is considered a catalyst of tetrathionate oxidation, the equilibrium and the final products will strongly depend on the composition of the solution (Varga and Horvath, 2007).

Various authors agree that the reaction order of tetrathionate in basic media is one (Rolia and Chakrabarti, 1982; Vongporm, 2008; Varga and Horvath, 2007; Zhang and Dreisinger, 2002). However, the reaction rate constant reported varies significantly among these authors, as shown in Table 13 and Figure 21.

Table 13.Summary of reaction rates reported for tetrationate at basic conditions

Author	Reaction Rate	Conditions		Comments
		pH	T (°C)	
Zhang and Dreisinger (2002)	$-\frac{d[S_4O_6^{-2}]}{dt} = 0.4\,M^{-1}s^{-1}[S_4O_6^{-2}]$	10	22	Reaction (40)
Varga and Horvath (2007)	$-\frac{d[S_4O_6^{-2}]}{dt} = 4.4x10^{-2}\,M^{-1}s^{-1}[S_4O_6^{-2}]$	9-12.2	25	Reaction (40)

Miranda-Trevino et al. (2009)	$-\frac{d[S_4O_6^{-2}]}{dt} = 6.1x10^{-3}M^{-1}s^{-1}[S_4O_6^{-2}]$	9	4-30	Initial rate method used Reaction (41)
Rolia and Chakrabarti (1982)	$-\frac{d[S_4O_6^{-2}]}{dt} = 5.1x10^{-3}M^{-1}s^{-1}[S_4O_6^{-2}]$	12	25	Reaction (41)

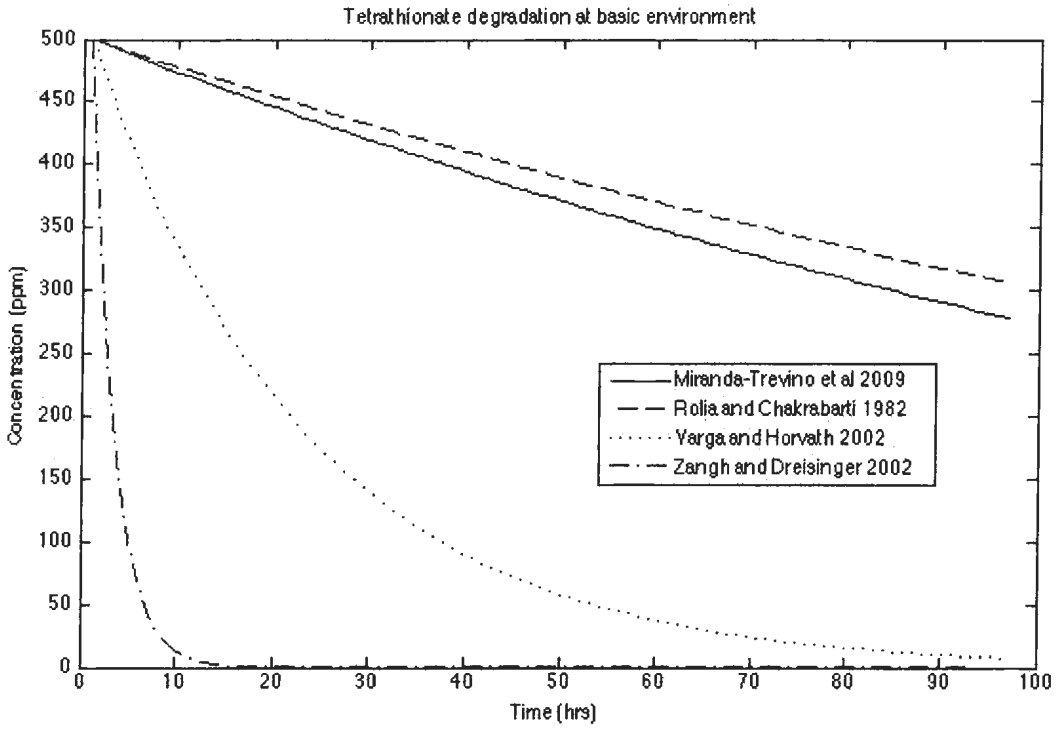


Figure 21 Degradation of Tetrathionate in basic environment

The strong dependency of the reaction on pH could be a partial explanation for the difference in the constants reported among different authors.

3.4.2 Tetrathionate and Pyrite reactions

Tetrathionate can be an important product of thiosulfate oxidation, for example, at low pH, in the presence of catalysts and as an intermediate in reactions involving pyrite (Druschell et al. 2003b; Xu and Schoonen, 1995). The formation rate of tetrathionate in

the presence of pyrite between pH of 2.2 and 6.9 has been described in the following way (Xu and Schoonen, 1995):

$$R^{n}_{S_4O_6} = K[FeS_2][S_2O_3^{2-}]^n \quad (42)$$

The reaction order *n* goes from one, at low thiosulfate/pyrite ratios, to zero (independent of the concentration), at high thiosulfate/pyrite ratios. The reaction constant is on average $6x10^{-8}$ Ms^{-1}. Mckibben (1984) studied the oxidation of pyrite at low pH and found that there was a significant amount of sulfur oxyanions, indicating the formation of a metastable compound which could be tetrathionate. Without the presence of catalysts, tetrathionate will be stable in acidic and neutral solutions (Xu and Schoonen, 1995) and will only react at high temperatures.

3.4.3 Tetrathionate and Iron (III) reactions

The reaction rate in the presence of Fe^{3+} with a pH<2 and T=70°C is given by Druschell et al., 2003a as:

$$r = 10^{-6.6\pm0.3}[Fe^{3+}]^{0.06\pm0.07}[S_4O_6^{2-}]^{0.3\pm0.08} \quad (43)$$

Druschell et al., 2003a suggested reaction 44 for the oxidation of tetrathionate in the presence of Fe^{3+} and oxygen after 100 minutes of progress; however, they also concluded that oxygen is a better oxidant than Fe^{3+} for tetrathionate.

$$4S_4O_6^{2-} + 3Fe^{3+} + 2.75O_2 + 4.5H_2O \rightarrow 4SO_4^{2-} + 3Fe^{2+} + 9H^+ \quad (44)$$

3.4.4 Tetrathionate and Hydrogen Peroxide reactions

The presence of hydrogen peroxide does not enhance the oxidation rate of tetrathionate (Druschell et al. 2003b). However, hydroxyl radicals do promote the oxidation, outlined by the following reactions:

$$S_4O_6^{2-} + 10H_2O \rightarrow 4SO_4^{2-} + 14e^- + 2OH^+ \quad (45)$$

$$OH^\bullet + 1e^- + H^+ \rightarrow H_2O \quad (46)$$

Druschell et al. (2003b) proposed an intermediate for the reaction of the form $HS_3O_4^{n-}$. This oxidation reaction can be considered to be second order with an equilibrium constant of the order of 10^8. The reaction pathway proposed is shown in Figure 21.

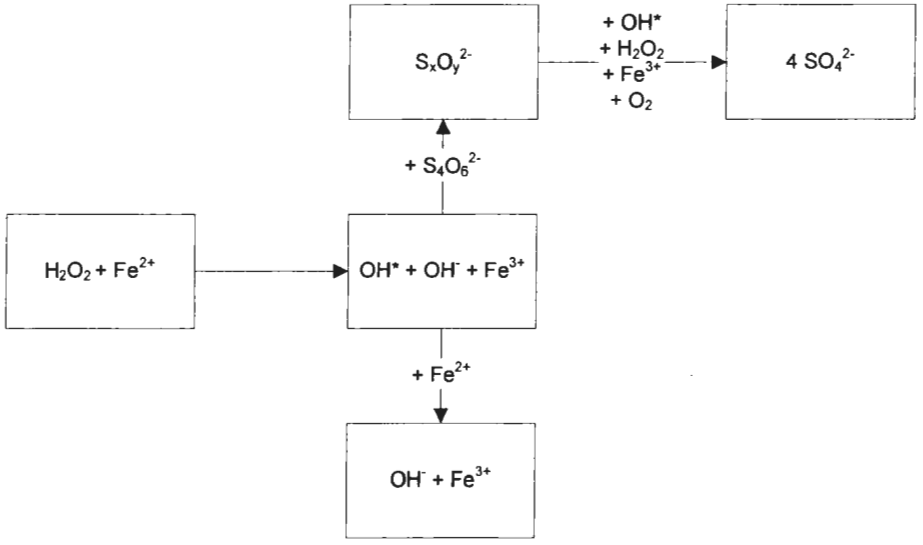


Figure 22 Reaction pathway for tetrathionate in the presence of Fe^{3+} at low pH (Modified from Druschell, 2003b)

In the case of basic environments, Voslar et al. (2006) identified thiosulfate as a key intermediate in tetrathionate oxidation by hydrogen peroxide according to the following reactions:

$$S_4O_6^{2-} + 2H_2O_2 + 4OH^- \rightarrow S_2O_3^{2-} + 4SO_4^{2-} + SO_3^{2-} + 4H_2O \quad (47)$$

$$S_4O_6^{2-} + SO_3^{2-} \rightarrow S_2O_3^{2-} + S_3O_6^{2-} \quad (48)$$

The time frame of these reactions is around 2 minutes. Sulfite can be further oxidized according to the conditions of the solution and could generate another sulfur intermediate such as trithionate. The reaction rate reported by Voslar et al. (2006) is:

$$-\frac{d[S_4O_6^{-2}]}{dt} = 1.5x10^2(M^2s)^{-1}[S_4O_6^{2-}][H_2O_2][OH^-] \quad (49)$$

3.4.5 Tetrathionate and Cu(II) reactions

Copper catalyzes tetrathionate degradation reactions at moderately high temperatures and low pH following a two stage process (Chanda and Rempel, 1987). The first stage involves the oxidation of thiosulfate and the formation of tetrathionate, following a pseudo first order reaction:

$$\frac{d[S_4O_6^{-2}]}{dt} = 0.5k_1[S_2O_3^{2-}] - k_3[S_4O_6^{2-}] \quad (50)$$

wherek_1 and k_3 depend on the catalyst and temperature according to Table 10. The second stage is the reaction of tetrathionate to form sulfate:

$$-\frac{d[S_4O_6^{-2}]}{dt} = k_3[S_4O_6^{2-}] \quad (51)$$

At high pH, tetrathionate reacts without the presence of catalysts, however, thiosulfate, which is stable in neutral and basic pH, acts as a catalyst for tetrathionate reactions (Chanda and Rempel, 1987; Moses et al., 1987).

3.4.6 Tetrathionate in the presence of microorganisms

The presence of microorganisms does enhance the oxidation of tetrathionate; depending on the type of bacteria present in the environment along with the temperature and dissolved oxygen conditions (Gould et al. 2004). *T. ferroxidans* and *T. thiooxidans* oxidize tetrathionate at pH between 3.5 and 4 and decrease the pH of the

solution to below 2. *T. thioxidans* oxidation rates are faster under these same pH conditions and a temperature of 25°C, this temperature is reported by Kupka et al. (2009) to be the optimal for tetrathionate degradation by *Thiobacillus*. At temperatures around 5°C, the oxidation of tetrathionate by the bacteria was slowed up to 360 hours. Wentzien et al. (1994) reported an optimal pH of 6.7 for *T. intermedius*.

Norlund et al. (2009) reported syntrophicsulfur processing between *T. ferroxidans* and *Ferroplasmaacidiphilum* which enhanced the generation of sulfuric acid from tetrathionate; however, no kinetic information is reported in the study. Although the reaction pathway for tetrathionate oxidation should yield sulfate as a final product, the results presented by Bernier and Warren (2007) indicates that an unidentified S species is the stable compound at pH below 2. The presence of trithionate is also reported by Wentzien et al. (1994) during a study of tetrathionate oxidation by *T. intermedius*.

In the presence of iron, some microorganism such as *Leptospirillumferroxidans*, do not oxidize the sulfur intermediates completely but other can achieve the complete oxidation like *T. ferroxidans* (Shippers et al., 1999).

3.4.7 Other tetrathionate reactions

Kerek and Horvath (2007) studied the oxidation of tetrathionate by iodine, proposing the following overall reaction after 4 hours of reaction progress:

$$S_4O_6^{2-} + 7I_2 + 10H_2O \rightarrow 4SO_4^{2-} + 14I^- + 20H^+ \qquad (52)$$

The reaction is independent of pH in the range of 4.25 – 5.55 and goes through an intermediate ion ($S_4O_6I^-$). The kinetics of this reaction is complex but the rate constant is in the order of 10^{-5}.

Read et al. (2001) studied the oxidation of tetrathionate by potassium ferrate. They found that the reaction mechanism changes above and below pH 8.6. Below that pH,

the reaction was pseudo first order but independent of tetrathionate concentration, while above pH of 8.6, the reaction was first order with respect to tetrathionate ions. The reactions rates are in the order 10^7 $Mhr^{-1}$and above.

4. Thiosalt Treatment Technologies

Thiosalts have become a concern for mining companies due to their potential toxicity (briefly discussed in Section 1.4) and pH depression (Dinardo and Sally, 1998). The current treatment strategy is to completely oxidize the sulfur oxyanions to sulfate. However, traditional wastewater treatment practices, such as alkali addition or natural degradation, are costly and unreliable in cold temperatures. (Wasserlauf and Dutrizac, 1982).

The specific conditions of the site have an important effect on the thiosalts chemistry and stability. Selecting the best treatment technology is site specific. Overall criteria for the comparison of treatment technologies are (Dinardo and Sally, 1998): installation cost, operational and maintenance cost, efficiency, technology availability and safety.

Kuyucak (1998) divided thiosalt treatment technologies into the following groups: 1) conventional, which includes the neutralization of the effluent by chemicals and the use of chemical reagents in general; 2) physic-chemical, which includes ion exchange, membrane process and solvent extraction; 3) biological, which includes wetlands, biological sulfates reduction and 4) passive, which includes the use of sulfate reduction bacteria (SRB), wetlands and anoxic limestone drains.

Another common subdivision of treatment technologies is simply active and passive treatments. Active treatment technologies would include the conventional, physic chemical and biological technologies in the subdivision made by Kuyucak (1998) and are characterized by the need of equipment, electrical power and specialized staff to run

these processes. On the other hand, passive technologies characteristics include the use of material native to the local environment, no need for electrical power and low operational and maintenance cost (Kuyucak, 2006).

4.1 Lime Neutralization Process

The neutralization process is not focused on the reduction of thiosalt concentration but rather neutralization of the acid already present and precipitation of metals such as Fe, Zn, Cu, Al and Pb according to the following general reaction (Kuyucak 1998):

$$Ca(OH)_2 + M^{2+}/M^{3+} + H_2SO_4 \rightarrow M(OH)_2/M(OH)_3 + CaSO_4 + H_2O \qquad (53)$$

The sludge formed due to the precipitation of the metals is separated through clarification where the suspended solids reach less than 1 mg/L. The residual sludge density varies from 1 to 30% solids (Kuyucak et al., 2001) however; a more advanced system such as high density sludge (HDS) can reach solids concentration between 60 to 70% (Kuyucak et al., 2001). Figure 23 shows a simplified diagram of a HDS process; the general operation principles of this process are the use of more than one neutralization reactor, the recycling of sludges clarification, aeration of the reaction and pH control.

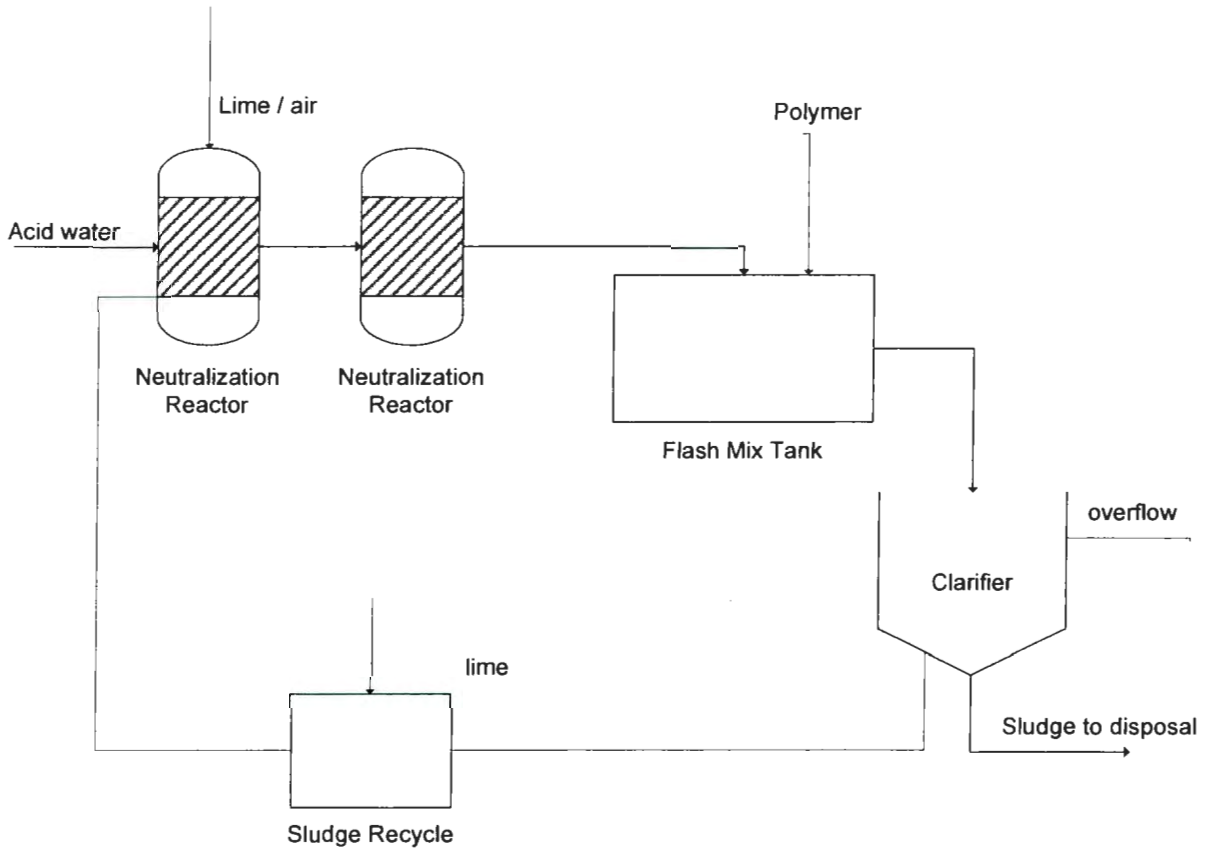


Figure 23 HDS process

Other compounds used for neutralization in addition to lime are:

- Limestone ($CaCO_3$) neutralization

Limestone is used to remove acidity and precipitate iron according to the following reactions (Kuyucak et al., 2001):

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + CO_2 + H_2O \quad (54)$$

$$3CaCO_3 + Fe_2(SO_4)_3 + 3H_2O \rightarrow 3CaSO_4 + 3CO_2 + 2Fe(OH)_3 \quad (55)$$

The produced CO_2 provides a buffer capability to the solution around pH 6.5, however, this also reduces the ability to precipitate other metals that require higher pH to

precipitate (Kuyucak et al., 2001). Negeri et al. (1999) shows that lime neutralization produces less thiosalts than other neutralization agents.

- Magnesium Hydroxide ($Mg(OH)_2$)

The buffer capability of magnesium hydroxide is around 9, hence it has the ability to precipitate a wider range of metals; it also produces a denser sludge which reduces the disposal cost. However, it's neutralization rate, however, is relatively slow in compare to the other chemicals (Kuyucak et al., 2001).

- Sulfides

Metals sulfides are usually less soluble than metal hydroxides. Depending on the condition of the effluent, they can provide some advantages for metal removal such as smaller sludge volumes and stability despite the pH change (Kuyucak et al., 2001).

During the precipitation process thiosalts can be removed as co-precipitants, as the study by Riveros and Chaulk (2000) demonstrated when they evaluated ferric salts as the coagulant. The co-precipitation depends of the thiosalt species and the metal/thiosalt ratio, with the affinity for co-precipitation as follows (Riveros and Chaulk, 2000):

$S_2O_3^{2-} > S_3O_6^{2-} > S_4O_6^{2-}$

4.2 Biological Reactors

Thiosalt oxidation by bacteria is highly influenced by environmental conditions; these conditions will determine the species and reactions pathways that the species will follow for their oxidation. Regardless of the species, the end product of the reaction is sulfateand pH depression, as in shown in Figure 5.

In general, *Thiobacillus*is linked to the oxidation of thiosalts at low pH, but several genus of the bacteria can be involved in the oxidation process according Table 14 (Dinardo and Sally, 1998).

Table 14 Species of Thiobacillus and their range for thiosalts oxidation (Modified from Dinardo and Sally, 1998).

Name	pH range
Thiobacillusthiooxidans	1.0 -6.0
Thiobacillusthioparus	~ 7.0
Thiobacillusneapolitanus	4.5 – 7.8
Thiobacillusnovellus	5.0 -9.5
Thiobacillusdenitrificans	6.0 -8.0

The principle of biological reactors is to use the oxidation capabilities of these bacteria to remove thiosalts from the effluent. The most common types of reactors are:

- Rotating Biological Contactor (RBC): The microorganisms are growth on the side of disks partially submerged in the effluent to be treated (Dinardo and Sally, 1998; Viessman and Hammer, 1993; Noyes, 1994). The disk rotates exposing the biofilms to the nutrients of the wastewater containing thiosalts or other contaminants and then to air. The excess microorganisms are washed out with the effluent and then could be precipitated in a subsequent step. Some of the advantages of this method are: low energy consumption, operational simplicity, high efficiency, low operation and maintenance cost and ability to compensate for changes in process conditions.
- Packed Bed Reactor: The reactor consists on a tank full of a material that increases the surface area for bacterial growth. The tank maintains a level of effluent similar to a plug flow pattern. Some of the advantages of this reactor include high retention time, good process control conditions, small space requirements, low maintenance and ability to accommodate flow fluctuations.

Pilot plants run by the Thiosalt Consortium on different sites have shown that the RBC was able to treat flows containing thiosalts up to 760 mg/L. However, the system experienced corrosion problems as well as operation and maintenance challenges (Dinardo and Sally, 1998). In their study, the packed bed reactor showed a better performance during the pilot tests reaching concentrations of less than 100 mg/L of total thiosalts from feeds with between 400 to 1200 mg/L thiosalts. The study by Dinardo and Sally (1998) reported technical and operation issues but did not specify their nature.

Advantages of biological reactors are cost efficiency, non-toxic by-products, safety to workers and environmental and energy efficiency. Disadvantages are the sensitivity to process variation, temperature dependency and lack of expertise with respect to biological systems in the mining industry. (Dinardo and Sally, 1998):

4.3 H_2O_2 / Ferric Sulfate

The objective of thiosalt treatment is to complete the oxidation of the sulfur intermediates to sulfate. Hydrogen peroxide (H_2O_2) is one of the strongest oxidizers available (Dinardo and Sally, 1998) and provides some advantages such as safe operations, non-toxic by-products, effective for year-round operations and dosage can be adjusted depending on the process.

The reactions with thiosalts are presented in sections 3.2.3 and 3.3.4. The oxidation rates with hydrogen peroxide are slow so the oxidant could decompose without attacking the sulfur intermediates; hence, the use of catalysts, such as ferric sulfate, is common to increase the rate of reaction (Druschell et al., 2003b). This technology has been adopted in recent years as the preferred method to treat thiosalts despite the cost associated with the use of H_2O_2 (Kuyucak, 2006). A general flow sheet of the process is presented in Figure 24.

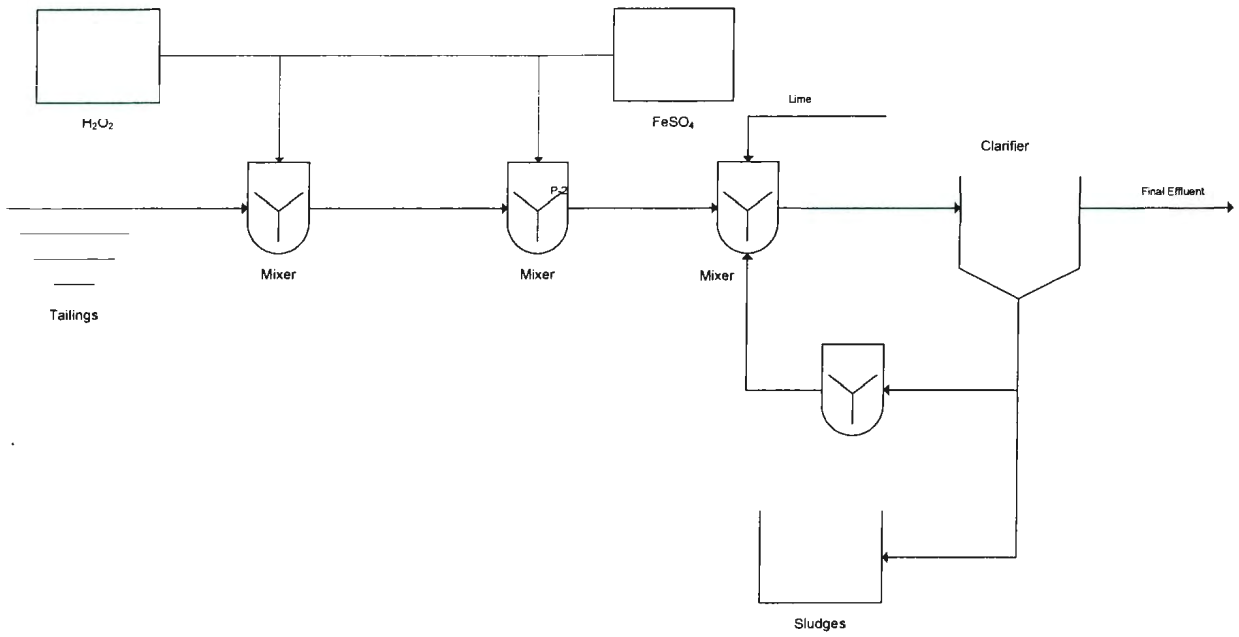


Figure 24 Hydrogen Peroxide Treatment Process (Modified from Dinardo and Sally, 1998)

In some of the waste streams, the addition of iron is not necessary as the concentration in tailings is enough to catalyze the oxidation of thiosalts (Druschell et al., 2003b). From laboratory tests, the mole ratio of thiosalts to hydrogen peroxide is 0.25 for thiosulfate, 0.5 for trithionate and 0.29 for tetrathionate. As a result of thiosalt oxidation and consequent pH depression, neutralization is a common step after the addition of hydrogen peroxide to the effluent.

This technology has been used to control thiosalt concentrations in effluent to levels below 10 mg/L. Some characteristics of the hydrogen peroxide treatment plant used by mining companies in the field are: consideration of natural degradation to reduce chemical consumption, seasonal operation of the equipment, use a fraction of the theoretical requirement from reaction stoichiometry, and control based on overflow from clarifiers and ponds (Fedath, 2009).

Dinardo and Sally (1998) suggest disadvantages for this treatment such as expensive reagents, additional steps needed to remove metals used as catalysts and that it is more a polishing step rather than a bulk treatment option.

4.4 Natural Degradation

Natural degradation is the conventional method for thiosalt treatment which involves the use of naturally present bacteria to degrade the sulfur intermediates (Dinardo and Sally, 1998; Gould et al., 2004). This process involves the use of long retention times, ideally up to one year, that will allow the oxidation to take place, but it is not effective year-round; especially in northern locations where biological activity decreases during winter (Dinardo and Sally, 1998).

Some mining companies have applied this treatment method to effluent discharges containing thiosalts with success. However, the average concentrations are usually below 200 mg/L and any modification in the thiosalt input or retention time will negatively affect the treatment (Nilsen, 2009). According to laboratory studies, the limiting factors for the natural degradation process are temperature and oxygen availability; while nutrients and bacteria population do not determine the efficiency of the process (Gould et al., 2004).

As a result of the thiosalt oxidation, this process requires pH control prior to final discharge. Other limitations of the technology are the use of large ponds to increase the retention time and the lack of control in the process. On the other hand, natural degradation should be an effective treatment during summer months, is relatively inexpensive and does not required extensive maintenance (Dinardo and Sally, 1998).

4.5 Wetlands

Wetlands are passive treatments with principles based on the use of native vegetation that support a variety of bacteria population that absorb or remove the contaminants.

Wetlands are divided in two areas: the oxidation zone, which is where there is the vegetation, and the reduction area where bacteria removes compounds such as sulfur, nitrogen and magnesium (Kuyucak, 1998)

There are two types of wetlands: free water surface flow and subsurface flow wetland. The first one resembles a natural wetland where the water runs through the vegetation but is exposed to the elements. The second type goes below a rock media, so exposure to the elements is not a variable in the process, however, the cost increases due to the placement of the rock. The efficiency of the wetland is based on retention time and the capability of the vegetation to treat the pollutants (Noyes, 1994). Some advantages of these systems are that they are easy to operate, maintenance costs are low and there is flexibility in their construction. On the other hand, drawbacks of this technology include the space required to construct the wetland and the potential for odour and insects if not properly managed.

Although the application of wetlands directly to thiosalt treatment has not been widely studied, it is an option worth exploring depending on the composition of the effluent and climate.

4.6 Electrochemical Oxidation

Electrochemical oxidation of thiosalts is achievable; however it is only economically feasible for low effluent volumes with thiosalt concentrations above 500 ppm (Dinardo and Sally, 1998). The main products of this process are sulfate and thiosulfate, yet the use of supplementary chemicals such as chlorine could prevent the generation of dithionate. As with most thiosalt treatment processes, there remains a need for neutralization after thiosalt oxidation. Some of the advantages of this process are that total thiosalt concentrations at discharge are below 10 mg/L, no chemicals are involved and treatment efficiency is high. However, some disadvantages are the high operational cost, the low cost-benefit for low concentration flows, lack of testing for operation at low temperatures and maintenance costs.

5. Discussion

The environmental impact of acid mine drainage from mining operations is a growing concern. Thiosalts have been identified to play an important role in the generation of those effluents; hence it is important to understand the reactions that cause pH depression in order to design adequate treatment technologies and evaluate the risk originated by these compounds. This paper summarizes studies related to thiosalts and mining during the last three decades in order to provide a starting point in future studies involving thiosalts.

The lack of regulation for thiosalts should not be interpreted as a sign of minimal environmental effects of these compounds. Although several acute toxicity studies for thiosalts have been inconclusive, the role of thiosalts in the generation of acid mine drainage and the subsequent problems generated are well document. In addition, new research is focusing on the effects that the pH depression due to thiosalts could trigger while in presence of other substances in the tailing ponds such as xanthates.

Thiosalt generation can occur during metal extraction process or during the oxidation of sulfide ores in tailings ponds. It is important to identify the conditions that promote their generation in the process, so those conditions could be avoided whenever possible. Nevertheless, the presence of thiosalts is expected in tailing ponds, therefore the knowledge of the pond conditions with respect to temperature, pH and reagents plays a key part in identifying the species and reaction pathways that these compounds could undergo before discharge.

A common practice in the industry is to measure the total thiosalt concentration by titration. This review summarize the importance of determining the specific thiosalt species present in the pond and exposes the reasons why measuring key sulfur species, especially thiosalts, is necessary for proper control of discharge and process optimization. The knowledge of the tailing pond conditions will be important to identify

the most important reactive species of thiosalts and their potential reaction pathways. As it shown in the paper, different species will react under different conditions. Hence treatment strategies must take into account thiosalt speciation, reagents (either present in the stream or to be added), pH and temperature.

Improvements in thiosalt treatment technology will result from a better understanding of the reaction pathways under process conditions. These improvements will lead to a minimization of pH depression in watersheds as a result of thiosalt discharge from mining operations.

Another objective of the paper is to identify the gaps in the thiosalt research to provide a path forward for future research. For example, past research has been focused on a narrow range of temperature and pH conditions and specific thiosalt species. As demonstrated in this paper, studies show that speciation and particularly the interplay between species, in addition to temperature and pH, are important in order to understand the reaction mechanisms of thiosalts.

Furthermore, knowledge of the kinetics and reaction mechanisms will be a great asset for improvement of treatment processes for these compounds in the tailings ponds. With respect to the mining and processing of sulfide minerals, the reaction pathways of the thiosalts are currently not well understood, and therefore, the design of any treatment system is limited with respect to efficiency. A detailed reaction mechanism identifying all intermediates and relative reaction rates is likely too complex to be determined accurately. However, a global mechanism that includes: rate limiting compounds, key intermediates, and contaminants of concern could be used to better design treatment systems and/or chemical application. The challenge ahead is to balance a model that contains enough information to explain the overallbehavior of thiosalts in ponds or treatment steps, and it is simple enough that can be applied in the mining industry.

The selection of the proper analytical technique is also important when dealing with thiosalts. Due to the rapid changes that could occur during their analysis, a quick and

reliable method should be selected. Capillary electrophoresis is an excellent analytical tool, providing good methods in terms of sensitivity for the different sulfur species, and more importantly in providing relatively quick analyses. Regardless of the method chosen, sample management is important for the success of thiosalt studies.

Data treatment in kinetic studies is important for the correct analysis and results evaluation. As a result of the diverse secondary reactions that occur during thiosalt oxidation, the initial rate method is a good starting point in terms of kinetic studies with thiosalt. However, additional thermodynamic information to determine equilibrium products should also be applied in the analysis.

The development of the kinetic model will be useful to help in varying the initial conditions in the tailing pond, to allow for risk characterization under the different scenarios proposed and to evaluate the efficiency of different treatment techniques. The environmental assessment study involving thiosalts should consider pH depression due to thiosalts, but also the secondary effects that this pH decrement could trigger in the water bodies such as metal leaching and mobilization.

A global mechanism for thiosalts oxidation could lead to a better understanding of the main reactions taking place and prediction of the relevant species present in the tailing ponds with specific conditions or over time. This information could be used in the mining process to reduce the generation thiosalt; in the treatment process to set up conditions that will drive equilibrium into the more stable species and finally in ponds to establish a more accurate environmental risk assessment and treatment strategy.

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Chapter 2

Effect of pH and Temperature on Thiosalt Reactions

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Abstract

Thiosalts are sulfur-oxygen compounds formed in the processing of sulfide minerals. In typical mining operations, thiosalts end up in the tailings ponds and may lead to pH depression in the discharged effluent as the thiosalts react to form sulfate. The presence of thiosalts in the pond is due to the inability of traditional treatment systems to either treat these compounds or their formation in the treatment, which is, in turn, a result of the lack of data on the reactivity of the various thiosalt species under pond conditions. In this study, the reaction rates of the three thiosalt species that predominant in mining effluent (thiosulfate, trithionate and tetrathionate) under pond conditions (experiments were done at pH range of 2 to 9 and temperatures between 4 and 30°C) were investigated. An equilibrium analysis was performed to inform experiments (e.g., species present and ultimate reaction products). Experiments were performed and reaction rate models were developed for each species.

1. Introduction

Inorganic sulfur compounds can be found in various oxidation states in the environment, with sulfate the most oxidized state (Suzuki, 1999). In the mining of sulfide minerals and processing of ores, partially oxidized sulfur compounds, thiosalts (which includes polythionates), can be formed (Wasserlauf and Dutrizac, 1982; Schipperset *al.*, 1996; Sasaki *et al.*, 1995; Paschka and Dzombak, 2004; Johnson, 2003). The stable species under typical tailing pond conditions are thiosulfate ($S_2O_3^{2-}$), trithionate ($S_3O_6^{2-}$) and tetrathionate ($S_4O_6^{2-}$) (Wasserlauf and Dutrizac, 1982). Natural sources of thiosalts include volcano crater lakes and excavation run-off (Brimblecome, 2005; Sriwanaet *al.*, 2000; Takano *et al.*, 1994). Another important source of thiosalts in the environment is the discharge from mining operations, especially those involving pyrite ores. Pyrite is the most common sulfide mineral in mining operations (Moses *et al.*, 1987) and therefore several authors have studied the oxidation of pyrite and the resulting sulfur compounds (Bordaet *al.*, 2004; Chernychova, 2003; Goldhaber, 1983; Mckibben, 1994;; Rimstidt and Vaughan, 2003, Schipperset *al.*, 1996). The oxidation products are a function of the temperature, pH, and oxidants involved. For example, at low pH, ferric ion (Fe^{3+}) is considered to be the key pyrite oxidant (Bordaet *al.*, 2004; Parshka and Dzombak, 2004; Johnson, 2003; Sasaki *et al.*, 1995; Moses *et al.*, 1987). Rimsdidt, (2003) proposed the following reaction pathway for pyrite oxidation:

$$FeS_2 \rightarrow FeS_2^{+} + e^{-} \quad (1)$$

$$FeS_2^{+} + H_2O \rightarrow FeS_2OH + H^{+} \quad (2)$$

$$FeS_2OH \rightarrow FeS_2O + e^{-} + H^{+} \quad (3)$$

$$FeS_2O \rightarrow FeS_2O_2 + 2e^{-} + 2H^{+} \quad (4)$$

$$FeS_2O_3 \rightarrow Fe^{2+} + S_2O_3^{2-} \quad (5)$$

However, thiosulfate is highly reactive under acidic conditions and will react to form tetrathionate (Shippers *et al.*, 1996a; Steudel, 1996):

$$2S_2O_3^{2-} + 2Fe^{3+} \rightarrow FeS_2O_3^{+} + FeS_2O_3^{+} \rightarrow 2Fe^{2+} + S_4O_6^{2-} \quad (7)$$

$$2S_2O_3^{2-} + \tfrac{1}{2}O_2 + 2H^{+} \rightarrow H_2O + S_4O_6^{2-} \text{ (pyritecatalyzed)} \quad (8)$$

At pH close to neutral, oxygen is considered to be the key oxidant (Parschka and Dzombak, 2004) according to the overall reaction:

$$FeS_2 + 3.5O_2 + H_2O \rightarrow Fe^{2+} + 2H^{+} + 2SO_4^{2-} \quad (9)$$

Negeri*et al.* (1999), and Rolia and Tan (1985) studied the key conditions and unit operations that promote the generation of thiosalts in the mining process. Their results suggest that in grinding and flotation, key factors in thiosalt formation are temperature, pH, residence time, dissolved oxygen and sulfur content in the ore. A pH range of 9.4 to 10.7 favors the generation of thiosalts (Rolia and Tan, 1985; Wasserlauf and Dutrizac, 1982), while an acidic to near neutral pH will inhibit formation (Rolia and Tan, 1985). Figure 1 shows a summary of the percentage of thiosalt generated in different parts of the process for two different types of ores.

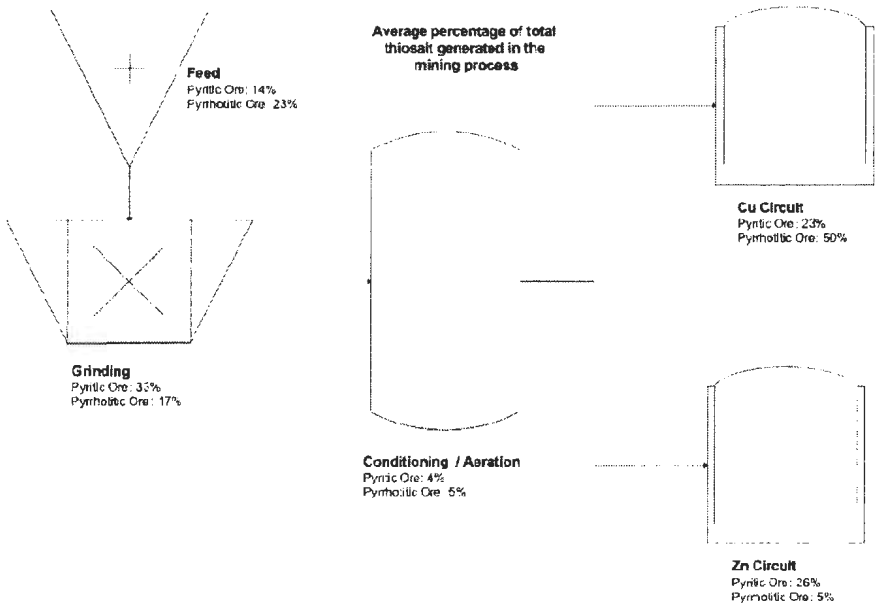


Figure 1 Average percentage of total thiosalt generated in the mining process (modified from Negeri*et al.* 1999).

The presence of sulfur compounds in mining waters may result in pH depression and mobilization of metals (Druschel*et al.*, 2004; Johnson, 2003). Concentrations of thiosalts in typical effluent from sulfide mineral mines can lead to pH depression from neutral conditions (pH ~ 8) to acidic conditions (pH~3) (Rolia and Tan, 1985) as well as high sulfate concentrations and metal loading (Tiwary, 2001). General consensus in the mining industry is that the main environmental consequence of thiosalts is the pH depression. Schwartz *et al.* (2006) and Yaschyhyn (2006) studied the acute toxicity of thiosalts to rainbow trout and *Daphnia Magna* and concluded that there is little to no impact on these species as a result of their exposure to thiosalt concentrations typical of mining effluents. However, the study revealed these species were susceptible to the resulting pH depression due to thiosulfate and tetrathionate oxidation.

The presence of bacteria, other sulfur compounds, temperature, and metals will also influence the thiosalt species distribution (Moses, 1987; Parschka and Dzombak, 2004; Shippers *et al.*, 1996a). Thiosalts reactions are complex as a result of the different

factors that affect them. Wasserlauf and Dutrizac (1982) identified the importance of the speciation of thiosalt and its effect on the different reactions that could occur. Table 1 shows a summary of thiosalt studies with the proposed reactions and experimental conditions.

Table 1. Summary of thiosalt studies and proposed reactions

Trithionate			
pH	**Temp (°C)**	**Reaction**	**Reference**
3.5 – 4.0	20 to 70	$3S_3O_6^{2-} \rightarrow S_4O_6^{2-} + {}^1/_8S_8 + 2SO_4^{2-} + 2SO_2$ $S_3O_6^{2-} \rightarrow {}^1/_8S_8 + SO_4^{2-} + SO_2$	Meyer and Ospina 1982
2.0 -4.0	70 to 110	$S_3O_6^{2-} + H_2O \rightarrow S_2O_3^{2-} + SO_4^{2-} + 2H^+$	Mizoguchi et al 1976
5.5 – 12.0	70 – 85	$S_3O_6^{2-} + H_2O \rightarrow S_2O_3^{2-} + SO_4^{2-} + 2H^+$	Rolia and Chakarabarti 1982
Alkaline	40 – 80	$S_3O_6^{2-} + 2OH^- \rightarrow S_2O_3^{2-} + SO_4^{2-} + 2H_2O$	Ahern et la 2006
>7.0	Not given	$2S_3O_6^{2-} + 2OH^- \rightarrow S_2O_3^{2-} + 4SO_3^{2-} + 3H_2O$	Wasserlauf and Dutrizac 1982
>12.0	Not given	$2S_3O_6^{2-} + 2OH^- \rightarrow S_2O_3^{2-} + SO_4^{2-} + H_2O$	Varga and Horvath 2007
>13.0	Not given	$2S_3O_6^{2-} + 6OH^- \rightarrow S_2O_3^{2-} + 4SO_3^{2-} + 3H_2O$	Varga and Horvath 2007
13.4 – 13.7	50	$S_3O_6^{2-} + 3H_2O \rightarrow S_2O_3^{2-} + 4SO_3^{2-} + 6H^+$	Ahern et la 2006
Tetrathionate			
1.0<	25-70	$2S_4O_6^{2-} \rightarrow S_5O_6^{2-} + S_3O_6^{2-}$	Druschel *et al.* 2003
1.0<	25-70	$S_4O_6^{2-} + H_2O \rightarrow SO_4^{2-} + S_3O_6^{2-} + 2H^+$	Druschel *et al.* 2003
1.0-2.0	130>	$4S_4O_6^{2-} + 5H_2O \rightarrow 2SO_4^{2-} + 7S_2O_3^{2-} + 10H^+$	Wasserlauf and Dutrizac 1982
2.0 -4.0	150 to 170	$3S_4O_6^{2-} + H_2O \rightarrow 7SO_4^{2-} + 7S + H^+$	Mizoguchi *et al.* 1976
3.5 – 4.0	20 to 70	$2S_4O_6^{2-} \rightarrow S_5O_6^{2-} + S_3O_6^{2-}$	Meyer and Ospina 1982
neutral	150>	$4S_4O_6^{2-} + 5H_2O \rightarrow 2SO_4^{2-} + 7S_2O_3^{2-} + 10H^+$	Wasserlauf and Dutrizac 1982
7.7 – 12.5	Not given	$S_4O_6^{2-} + SO_3^{2-} \rightarrow S_2O_3^{2-} + S_3O_6^{2-}$	Zhang and Dreisinger 2002

9.2 – 12.2	25	$2S_4O_6^{2-} + 6OH^- \rightarrow 3S_2O_3^{2-} + 2SO_3^{2-} + 3H_2O$	Varga and Horvath 2007
11.5	22	$2S_4O_6^{2-} + 6OH^- \rightarrow 3S_2O_3^{2-} + 2SO_3^{2-} + 3H_2O$	Zhang and Dreisinger 2002
11.5	22	$10S_4O_6^{2-} + 34OH^- \rightarrow 13S_2O_3^{2-} + 38/3SO_3^{2-} + 3H_2O + 4/3S^{2-}$	Zhang and Dreisinger 2002
12.0	25	$4S_4O_6^{2-} + 6OH^- \rightarrow 5S_2O_3^{2-} + 2S_3O_6^{2-} + 3H_2O$	Rolia and Chakarabarti 1982
Thiosulfate			
<2.3	70 – 150	$5S_2O_3^{2-} + 6H^+ \rightarrow 2S_4O_6^{2-} + 2S^o + 3H_2O$	Mizoguchi *et al.* 1976
<2.3	70 – 150	$S_2O_3^{2-} + H^+ \rightarrow HSO_3^- + S^o$	Mizoguchi *et al.* 1976
<2.3	70 – 150	$3S_2O_3^{2-} + 2H^+ \rightarrow 2SO_4^{2-} + 4S^o + H_2O$	Mizoguchi *et al.* 1976
Acidic	Not Given	$2S_2O_3^{2-} + 2H^+ + ½\ O_2 \rightarrow S_4O_6^{2-} + H_2O$	Wasserlauf and Dutrizac 1982
2.0 – 4.0	150	$2S_2O_3^{2-} + 2H^+ \rightarrow SO_4^{2-} + H_2O$	Wasserlauf and Dutrizac 1982
2.9	25	$2S_2O_3^{2-} + H^+ \rightarrow HSO_3^- + SO_3^{2-} + 2S^o$	Xu and Schoonen 1995
Not Given	25 – 32	$2S_2O_3^{2-} + H_2O \rightarrow HS^- + SO_4^{2-} + 2H^+$	Jorgensen 1990
Basic	125	$S_2O_3^{2-} + 2O_2 + H_2O \rightarrow 2SO_4^{2-} + 2H^+$	Rolia and Chakrabarti 1982

Most of the studies in Table 1 were conducted over limited pH ranges or temperatures higher than typical conditions in the effluent pond. The thiosalt reactivity in the pond is critical, as it will determine the water quality and therefore the impact on receiving water bodies. Experiments done by Vongporm (2008) at temperatures between 4 to 30°C and pH between 2 and 9 show the relationship between temperature and pH and speciation by identifying the conditions in which each of the three main species (thiosulfate, trithionate and tetrathionate) are reactive (Figure 2).

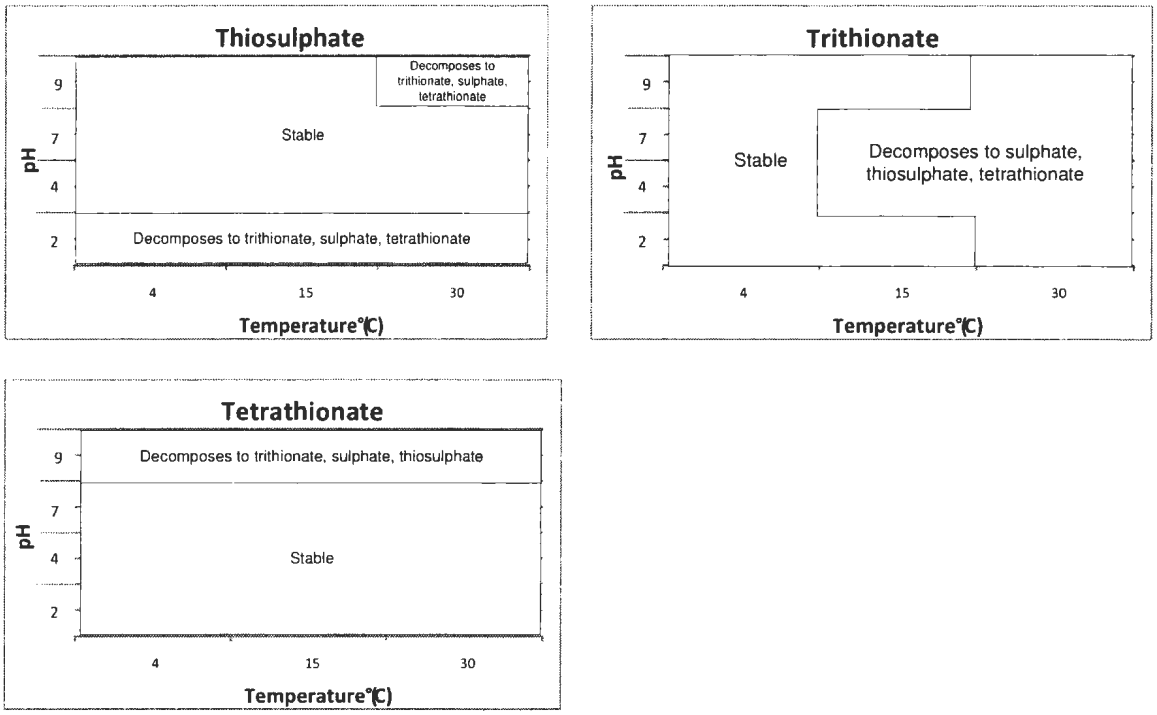


Figure 2 Reactive conditions for thiosalts (Modified from Vongporm, 2008)

The lack of data on thiosalt reaction rates and speciation in the pond has typically resulted in over-treatment of effluent to oxidize the thiosalts and then neutralize the effluent. This results in increased costs due to excessive chemical use and sludge generation, thereby decreasing much of the environmental benefit. It is apparent that reaction rates and information regarding speciation is required in order to design and develop effective thiosalt management systems.

Due to the reactivity of thiosalts, assessing reaction rates is challenging and requires a rigorous experimental protocol. As such, prior to reaction rate experiments, in this work we established a sample management program to ensure samples reflected the conditions at the time of sampling. This protocol is outlined in the experimental section.

2. Research Strategy and Experimental Methods

To determine relative reaction rates, batch experiments were performed under pH and temperature conditions typical of effluent ponds; details and the specific sampling protocol are outlined in Section 2.1. The analytical advantages and protocol using capillary electrophoresis are explained in the analytical method section. Finally, in Section 2.3, the approach taken to analyze the kinetic data and additional simulations done in HSC to obtain equilibrium information are explained.

2. 1 Batch Studies

In the case of the kinetic studies under batch conditions, thiosalts are known to catalyze their own degradation reactions (Wasserlauf and Dutrizac, 1982), adding complexity to their study. To simplify the global reaction mechanisms, each thiosalt was studied independently; data obtained was used in the development of global reaction rates.

Three thiosalt were studied: thiosulfate, trithionate and tetrathionate. Sodium thiosulfate penta-hydrate was purchased from Merck and potassium tetrathionate from Sigma-Aldrich were used during the experiments. Trithionate is not commercially available and was synthesized using a modified method from Kelly and Wood (1994). The pH of the solutions was maintained using buffer solutions, except for pH 2, where the pH was adjusted only with acid. For pH 2 the buffer was acetic acid: glacial acetic acid diluted to pH 2; pH 4 used 50 mM ammonium acetate/acetic acid; pH 7 the buffer was 50 mM ammonium dihydrogenphosphate/ ammonium hydrogenphosphate and for pH 9 a 50 mM ammonium acetate/ ammonium hydroxide buffer was used.

As previously indicated, the experimental conditions reflected the effluent treatment/pond conditions as outlined in Table 2.

Table 2. Experimental conditions

Variables	Levels
Thiosalt	Thiosulfate, Trithionate, Tetrathionate
Temperature (°C)	4, 15, 30
pH	2, 4, 7, 9
Concentration (mg/L)	250, 500, 1000
Time	0 to 72 hours

Batch studies were conducted in the laboratory using solutions made by dissolving accurately weighed portions of each thiosalt species in 100 mL of the appropriate acid or buffer solution. Each of these were transferred to 250-mL volumetric flasks, sealed with a stopper, and agitated at the temperature of study. 1.5-mL samples were taken at specific times, filtered using a 0.2 µm nylon filter and stored until analysis. Due to the reactivity of some species in certain conditions, sample management in the lab was extremely important to avoid further reaction while the sample is waiting to be analyzed (Vongporm, 2008). The sampling protocol was as follows (Vongporm, 2008): filter sample and immediately flash-freeze in liquid nitrogen, store at -80°C until analysis. Prior to analysis, samples are transferred from the ultralow freezer (-80°C) to a regular freezer (-4°C) on the day of analysis and allowed to thaw for only 10 minutes before analysis.

2.2 Analytical Method

Analysis was done using an Agilent Capillary Electrophoresis (CE) system (Model 1602) with UV detection. The capillary (Microsolv Technology Corporation) was a base fused silica with polyimide coating, 50 µm inner diameter, 48.5 cm total length and 40 cm effective length (length to the detection window). The background electrolyte (BGE)

used was pyromellitic acid (chromophore), hexamethonium bromide (EOF modifier) and Triethanolamine (for pH adjustment)and filtered with a 0.2 µm nylon filter before use. The sample was placed on a 1 mL polypropylene vial with polyurethane snap cap. The operational procedure for the CE was: flush capillary with 0.1 M aqueous sodium hydroxide for 15 min, followed by BGE for 10 min; sample hydrodynamically injected with 50 mbar for 10 seconds, analysis by capillary zone electrophoresis was carried out using an applied voltage of 30 kV with negative polarity. The capillary was contained in a cassette that was air-cooled at 23°C. The detection wavelength for thiosulfate and tetrathionate: 214 nm and trithionate: 194 nm.

CE has several advantages over other methods used in thiosalt analysis, for example, analysis is rapid (5 minutes for most common thiosalts (Pobozy*et al.*, 2002)), anion separation efficiency is very good, operation cost are low, and analysis can be carried out using small volumes of sample and reagents (Haddad, 1997; Motellier and Descostes, 2001). In comparison with other techniques such as ion chromatography, CE does only have a moderate sensitivity that can be partially overcome by the selection of an adequate background electrolyte (BGE) and the use of indirect methods (Padarauskas*et al.*, 2000).

2.3 Equilibrium Analysis and Determination of reaction rates.

Reaction equilibrium analysis is a useful tool for validating trends in experimental data or models and identifying key reactants/products for analysis. The theoretical concentration at equilibrium for individual thiosalt species and mixtures was calculated with the Gibbs energy minimization approach using the HSC Chemistry software V7.0 from Outotec. The simulations were done assuming one liter of solution and a dissolved oxygen concentration of $1x10^{-5}$kmol. Thiosalt reactivity is governed predominantly by pH and presence of oxidizers, and, to a lesser extent, temperature over the range of pond conditions studied (Vongporm, 2008). As such, in these calculations the pH of the solution to be studied was set and the equilibrium analyzed from 4 to 30°C.

The reaction rate was derived using the initial rate method that is based on the principle that the kinetic information gathered in the initial stages of the reaction should apply until equilibrium is reached (Mortimer and Taylor, 2002). Equation 1 represents the differential equation that follows the change in concentration with time:

$$\frac{d[C]}{dt} = K[C]^n \quad (1)$$

Where K is the reaction constant, n is the reaction order, C is thiosalt concentration in mmol L^{-1} and t is time in hrs.

Thiosalt reactivity varies with temperature, initial concentration and pH conditions. Hence, values for the two variables (K and n) of Equation 1 should be estimated by fitting measured data from experiments performed under different combinations of these parameters. This fitting problem is over-determined, and thus vastly different values of K and n can provide equally good fits to the experimental data. To obtain a meaningful physical result, the optimization has to be constrained to thermodynamically realistic values.

Our approach used a two-step sequential optimization. The first step was an exhaustive search of K and n values over a discrete range of values (n had a range between 0 and 3 and K from 0 to 1). We used an explicit Runge-Kutta approach (the RK4 method ode45 in Matlab) to numerically solve Equation 1 for each (K,n) pair, and each set of initial conditions and pH values. The numerical solutions of the ordinary differential equation (ODE),were then compared to the corresponding experimental data to see which values of K and n provided the smallest least-square error. In the second step, we used the Matlab constrained minimization method fmincon to refine the estimates of K and n, beginning from the best values found in step 1. In both steps the simulations were done only under conditions where thiosalts are reactive.

3. Results

3.1 HSC Simulations

Equilibrium analysis provides final product distribution for a batch reaction based on a Gibbs free energy minimization approach and the databases provided. The HSC software provided the product distribution over the pH and temperature range of the study. The initial concentration of specific thiosalt species was set at 1000 mg/L. In this approach, the user must specify possible products based on prior knowledge of the system, in this work it was based on previous experiments (Vongprom, 2008) and reports from the literature. Table 3 presents the results of the simulations under reactive conditions of each thiosalt. (Vongprom 2008), It was clear that for the time scales we studied previously (Vongprom, 2008), thiosulfate was unreactive at pH greater than 4 and tetrathionate was not reactive at pH less than 9, as such the equilibrium analysis was performed for thiosulfate at pH of 2 and tetrathionate at pH of 9.

The equilibrium analysis indicates the main sulfur species are hydrogen sulfide, elemental sulfur and sulfate. Sulfate is the main product of thiosalts reactions in the conditions; elemental sulfur is also present and its amount depends on which thiosalt is input initially. Sulfur concentrations were 167 mg/L with thiosulfate as the initial species, 115 mg/L with tetrathionate, while trithionate produced 8 mg/L S for the equilibrium concentration.

Table 3 Sulfur Species at Equilibrium as result of the HSC simulation

Reactant	Product distribution at equilibrium (% of total Sulfur in the sample)			
	pH = 2	pH = 4	pH 7	pH = 9
Thiosulfate	H_2S (0.01%) S^o (29.2%) SO_4^{2-} (70.7%)	Not reactive under these experimental conditions over the time interval studied of 96 hours		
Trithionate	H_2S (0.01%) S^o (1.7%) SO_4^{2-} (98.29%)	H_2S (0.01%) S^o (1.7%) SO_4^{2-} (98.29%)	H_2S (0.01%) S^o (1.7%) SO_4^{2-} (98.29%)	H_2S (0.01%) S^o (1.7%) SO_4^{2-} (98.29%)
Tetrathionate	Not reactive under these experimental conditions over the time interval studied			S^o (20.4%) SO_4^{2-} (79.5%)

3.2 Material Mass Balance

The material balance for sulfur and oxygen for thiosulfate, trithionate and tetrathionate is presented on Table 4 for the results obtained in the lab at 72 h, and the results of the equilibrium simulations using an initial concentration of 1000 mg/L for each of the thiosalts.

Table 4 Sulfur and oxygen material mass balance for the three main sulfur species.

Thiosulfate as initial thiosalt

		Sulfur (mmol)			Oxygen (mmol)		
		@0 hrs	@ 72 hrs	@Equilibrium	@0 hrs	@ 72 hrs	@Equilibrium
pH 2	S_2O_3	17.8	3.9	---	26.7	5.9	---
	S_3O_6	---	2.1	---	---	4.1	---
	S_4O_6	---	0.4	---	---	0.6	---
	SO_4	---	0.6	12.5	---	2.5	50
	S°	---	n/a	5.2	---	---	0
	Total	17.8	7	17.7	26.7	13.1	50

Trithionate as initial thiosalt

		Sulfur (mmol)			Oxygen (mmol)		
		@0 hrs	@ 72 hrs	@Equilibrium	@0 hrs	@ 72 hrs	@Equilibrium
pH 2	S_2O_3	---	0.7	---	---	1.1	---
	S_3O_6	15.9	12.6	---	31.8	25.2	---
	S_4O_6	---	0.2	---	---	0.3	---
	SO_4	---	0.8	15.5	---	3	62
	S°	---	n/a	0.4	---	---	0
	Total	15.9	14.3	15.9	31.8	29.6	62

Trithionate as initial thiosalt

		Sulfur (mmol)			Oxygen (mmol)		
		@0 hrs	@ 72 hrs	@Equilibrium	@0 hrs	@ 72 hrs	@Equilibrium
pH 4	S_2O_3	---	2.7	---	---	4	---
	S_3O_6	15.9	11.8	---	31.8	23.5	---
	S_4O_6	---	0.1	---	---	0.2	---
	SO_4	---	1.4	15.5	---	5.6	62
	S°	---	n/a	0.4	---	---	0
	Total	15.9	16	15.9	31.8	33.3	62

pH 7	S_2O_3	---	2.6	---	---	3.9	---
	S_3O_6	15.9	11.6	---	31.8	23.2	---
	S_4O_6	---	0.3	---	---	0.4	---
	SO_4	---	1.5	15.5	---	5.9	62
	S°	---	n/a	0.4	---	---	0
	Total	15.9	16	15.9	31.8	33.4	62

Tetrathionate as initial thiosalt

		Sulfur (mmol)			Oxygen (mmol)		
		@0 hrs	@ 72 hrs	@Equilibrium	@0 hrs	@ 72 hrs	@Equilibrium
pH 9	S_2O_3	---	4.7	---	---	7	---
	S_3O_6	---	2.9	---	---	5.9	---
	S_4O_6	17.6	8.3	---	26.4	12.4	---
	SO_4	---	0.2	14	---	0.9	56
	S°	---	n/a	3.6	---	---	0
	Total	17.6	16.1	17.6	26.4	26.2	56

Trithionate as initial thiosalt

		Sulfur (mmol)			Oxygen (mmol)		
		@0 hrs	@ 72 hrs	@Equilibrium	@0 hrs	@ 72 hrs	@Equilibrium
pH 9	S_2O_3	---	1.8	---	---	2.8	---
	S_3O_6	15.9	13.4	---	31.8	26.8	---
	S_4O_6	---	0.1	---	---	0.2	---
	SO_4	---	1.8	15.5	---	7	62
	S°	---	n/a	0.4	---	---	0
	Total	15.9	17.1	15.9	31.8	36.8	62

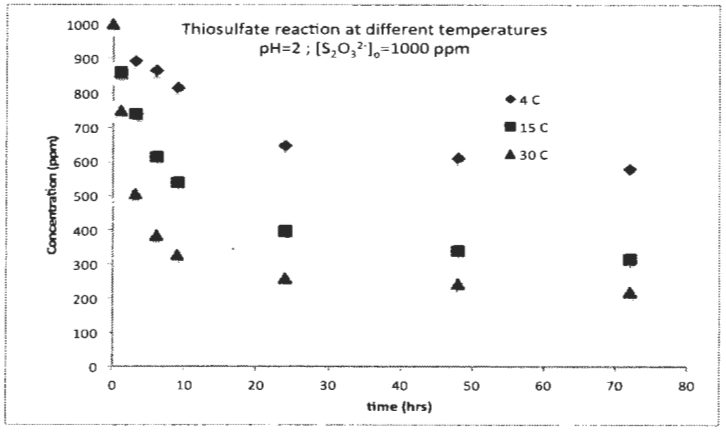
Most of the sulfur remains in solution in all cases except for thiosulfate at pH 2, where the unaccounted for sulfur could be due to the precipitation of elemental sulfur, generation of hydrogen sulfide or, under saturated conditions, sulfite (not measured in this work). For trithionate and tetrathionate, most of the sulfur can be found in solution in any of the forms followed in the lab. A key factor is the amount oxygen required to achieve the concentration of the various sulfur species at equilibrium. Oxygen from the thiosalts alone would not be enough to achieve these concentrations, where in some cases the oxygen demand calculated from the amount of oxygen in the equilibrium products is double the initial oxygen in the thiosalts. Thus, some oxygen must come from that dissolved in the solution. Xu and Schoonen (1995) reported that the lack of oxygen in solution would not affect the reaction rate of thiosulfate but only the end products, which is supported by the kinetics results presented next.

3.3 Experimental Results

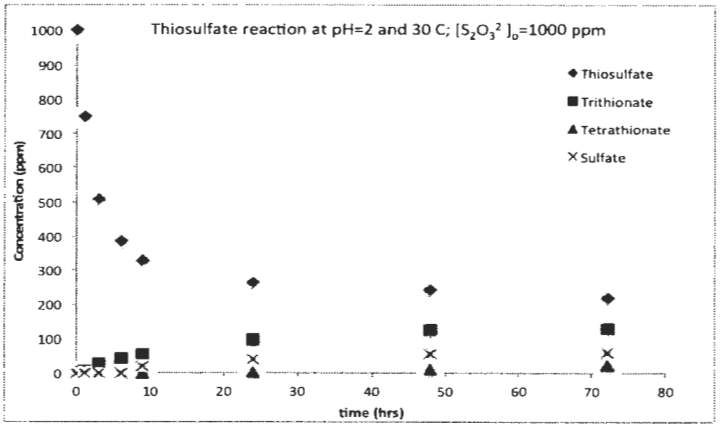
Thiosalt reactivity depends on the temperature, pH and the species present in solution (Figure 2). In this study, the focus has been on timescales relevant to the pond and treatment systems, therefore the longest experiment lasted 96 hours. Wasserlauf and Dutrazic (1985) performed experiments over weeks and showed reactions continue at a very slow rate after the first 2-3 days.

The experimental results for the transformations of the thiosalts over time and under various conditions are summarized in Figures 3 to 5. Thiosulfate is reactive at pH 2 and reactivity increases with temperature (Fig. 3.a). Thiosulfate concentration drops for the first 24 hours and then the degradation slows down and remains relatively constant until the end of the interval of interest (72 h).,. This data was used in the calculation of activation energy for the reaction at pH 2. However, it was not possible to include a pH parameter for the kinetic model, as thiosulfate was unreactive in the time scales in these experiments for higher pH values. The greatest rate of change for thiosulfate concentration occurs, somewhat predictably at 30°C. At this temperature and pH, the

production of the other thiosalt species is also highest (Figure 3.b). Trithionate and sulfate are the main products, with traces of tetrathionate also apparent. By 72 h the reaction has not reached concentrations predicted by HSC equilibrium calculations, but the change in concentration is small and within experimental error so it is hard to visualize any significant change.



a)



b)

Figure 3. Change of thiosulfate concentration with time. (a) as a function of temperatures and (b) Change is sulfur species.

Trithionate showed reactivity over the entire pH range, which differs from thiosulfate and tetrathionate. The experimental data shows that trithionate reacts faster at neutral or slightly acid conditions than at basic conditions. The activation energy was calculated using data from other kinetic studies (Meyer and Ospina, 1982) under the same pH conditions but at different temperatures as shown in Figure 9. Unlike thiosulfate, the reaction of trithionate appears to continue to react past 72 h.

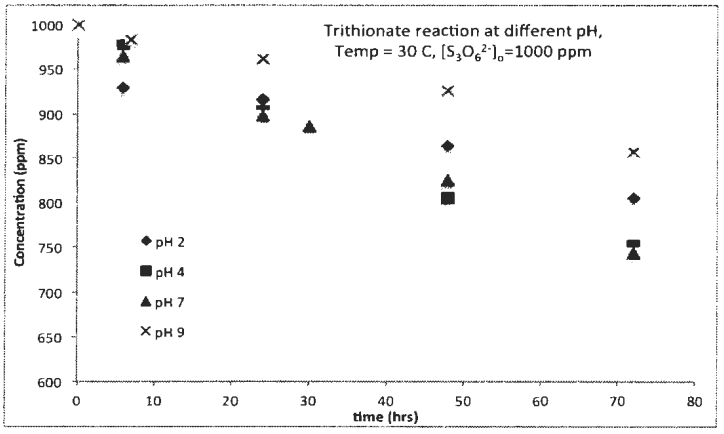
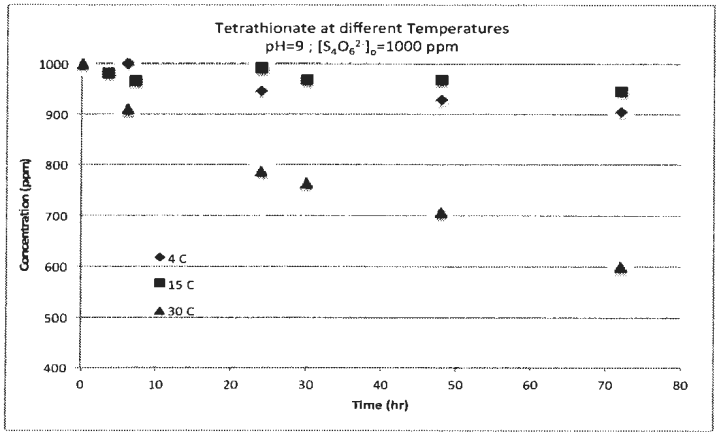
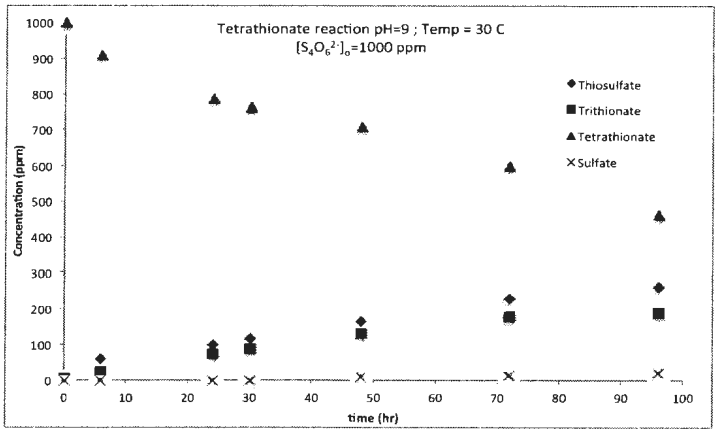


Figure 4. Change of trithionate concentration with time as a function of pH.

Tetrathionate experiments show increases in reactivity with increased temperature under alkaline conditions, with a large drop in concentration in experiments conducted at 30°C. The main species present during the reaction are thiosulfate and trithionate with traces of sulfate at pH 9. Similar to trithionate, tetrathionate reaction continues to at least past our experimental run times.



a)



b)

Figure 5. Change of tetrathionate concentration with time. (a) As a function of temperatures and (b) Concentration of sulfur species with time.

Figure 6 compares the results for the experimental data in the kinetics studies and equilibrium simulations done in HSC software, which strictly describes the speciation at equilibrium (infinite equilibration time). During the equilibrium simulations at all pH values, the main final product was sulfate, however, during the timeframe of the experiments, other sulfur species, mainly thiosalts, dominated the product composition in solution. The HSC experiments were initiated to establish the likely composition of a reaction mixture at equilibrium based on first principle of thermodynamics, as a rationale for the choice of species to monitor in experimental work. Differences between

equilibrium calculations and experimental results are not unexpected, and provide a measure of reaction progress, which in this case is far from the final equilibrium products.

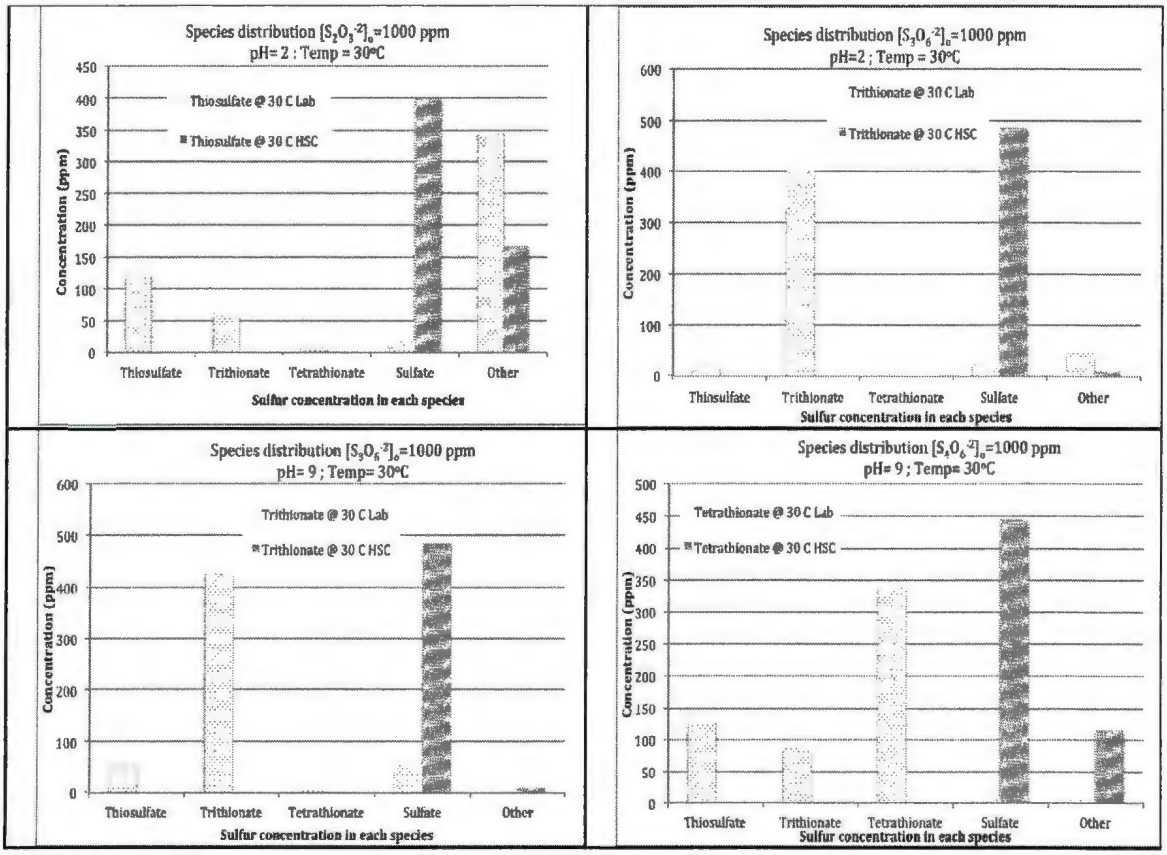


Figure 6. Comparison between product speciation obtained in HSC simulations and lab experiments. For the lab experiments, the initial concentration of the indicated thiosalt was 1000 mg/L and analysis was complete after 72 h. In HSC, the simulations used an initial concentration of 1000 mg/L of the thiosalt.

Elemental sulfur and hydrogen sulfide were not measured in this work, however, the elemental sulfur was observed visually as a pale yellow precipitate in thiosulfate solutions at acidic pH. Under those conditions, the characteristic odor of H_2S was also

noted, but was present at concentrations low enough that they did not trigger the H_2S monitor.

3.4 Kinetics Results

Using the initial rate method, kinetic rate expressions were developed for each thiosaltspecies. As has been reported previously, thiosalt speciation depends on pH and temperature conditions of the solution. A summary of the results for each thiosalt is presented next. The reaction order was determined from the experimental data using a van't Hoff plot for the experiments at each of three temperatures of interest. Using reaction order from these results, Equation 1 was optimized using experimental data, least squares regression and the Runge-Kutta approach, which is explained in detail by Hairer*et al.* (1989). The simulation was performed only in reactive conditions and the results were then compared to published data.

3.4.1 Thiosulfate Results

Van't Hoff plots for thiosulfate for data at 4, 15 and 30°C are shown in Figure 7. The plots are at pH 2.

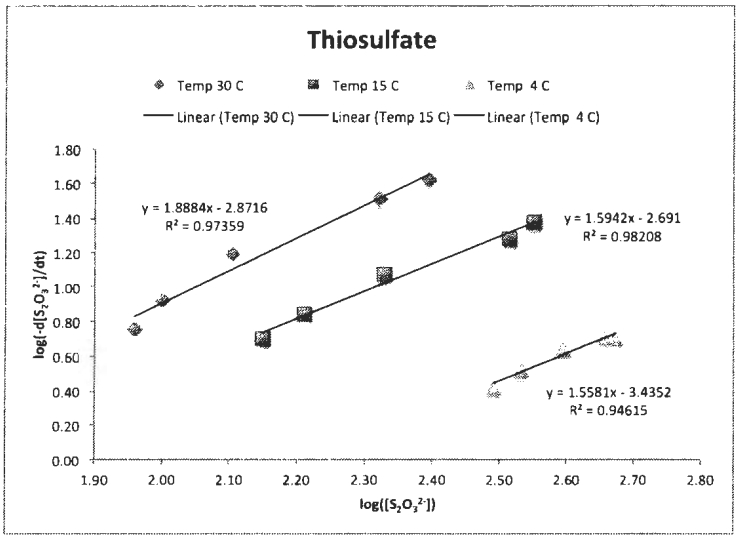


Figure 7.Van't Hoff plots for thiosulfate at different temperatures.

The slope of the Van't Hoff plot is related to the reaction order. In the temperature range of 4 to 30℃, the slope varies from 1.55 to 1.88, which is close to the reaction order of two proposed by Xu and Schoonen (1995). The optimization was constrained between 1.55 – 2 and the results are presented in Table 5.

Table 5. Results for thiosulfate optimization for reaction order of two

Reference	pH	Temp (℃)	K (x10^2)	n
Current Experiment	2	4	0.24	2
Current Experiment	2	15	1.20	2
Current Experiment	2	30	3.00	2
Xu and Schoonen (1995)	2.9	20	2.86	2

The reaction constant increased with temperature as expected. Data from theXu and Schoonen (1995) experiment was also included in the simulation to obtain the reaction constant at their conditions of pH 2.9 and temperature of 20℃. The Arrhenius plot for thiosulfate is shown in Figure 8.

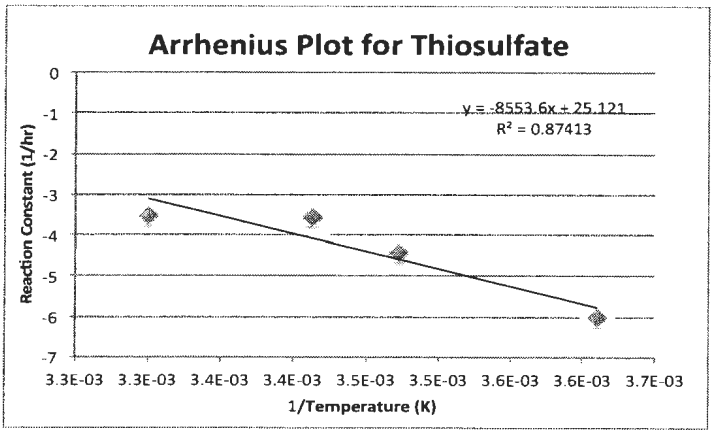


Figure 8. Arrhenius plot for Thiosulfate

Figure 8 shows that the activation energy (E_a) for thiosulfate, in a pH range of 2 to 2.9 and a temperature range 4 to 30°C, is 71.1 kJ and the Arrhenius constant is 8.7×10^{10}. Substituting those values in the following equation, a parity plot is shown in Figure 9.

$$\frac{\delta[S_2O_3^{2-}]}{\delta t} = A_0 e^{\frac{-E_a}{RT}}[H^+][S_2O_3^{2-}]^2 \qquad (2)$$

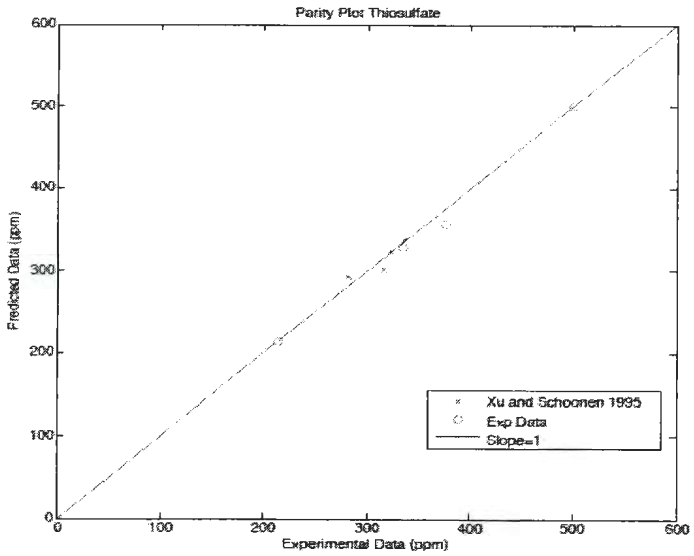
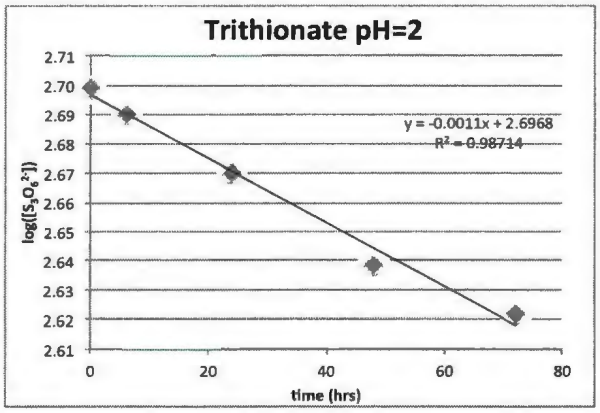


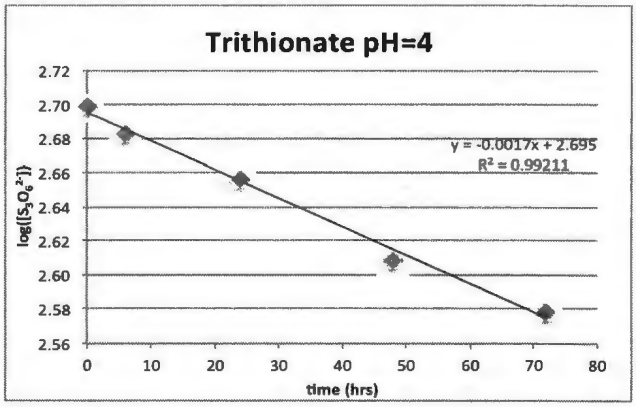
Figure 9. Parity Plot for thiosulfate

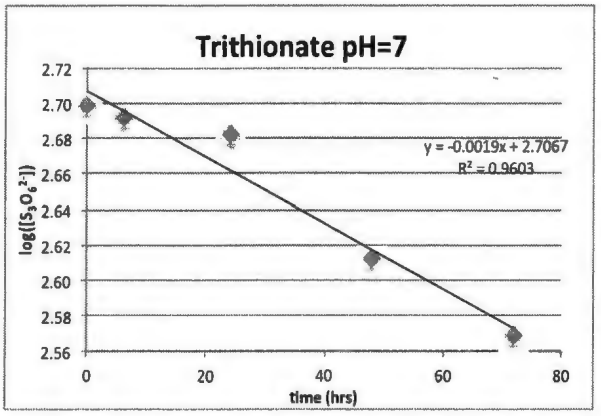
The model prediction follows experimental data as shown in the parity plot for our experimental data and that of Xu and Schoonen (1995) for data up to 25 hours. This confirms that thiosulfate reaction at low pH follows a second order rate constant and that the rate can be corrected depending on the pH of the solution. This is a significant advantage of using Equation 2, as the reaction rate proposed includes dependence for both temperature and pH. Xu and Schoonen (1995), proposed the presence of elemental sulfur and sulfite in the thiosulfate reaction at low pH; in our experiments sulfur was present as precipitate, hydrogen sulfide was detected qualitatively, and sulfite was not measured.

3.4.2 Trithionate Results

Trithionate is the only species in the study reactive over the range of pH. The Van't Hoff plot for the experimental data shown in Figure 10 indicates a reaction constant of one, which is the same as proposed by Ahern (2006) and Meyer and Ospina (1982).







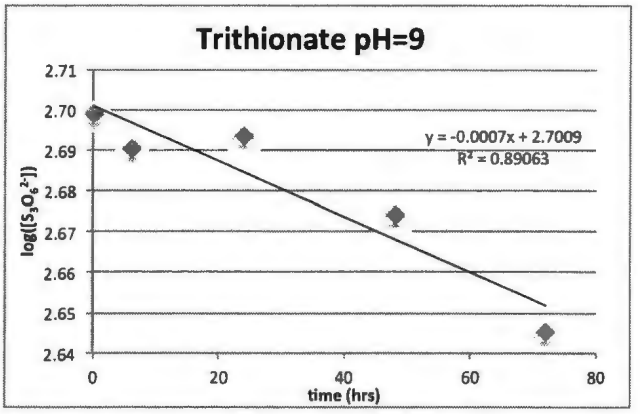


Figure 10. Van't Hoff plots for Trithionate

Table 6 shows the results of the optimization routine, fixing the reaction order at one

Table 6 Optimization results for trithionate at 30°C

pH	K ($x10^3$)	N
2	2.6	1
4	4.1	1
7	3.9	1
9	4.1	1

From Table 6, the value of the reaction constant for trithionate at 30°C seems to be independent of pH, especially in the range of 4 to 9. This means that Equation 3 will not include a term for protons or hydroxyl ions. Figure 11 compares the results for trithionate degradation at pH 2 and the model values.

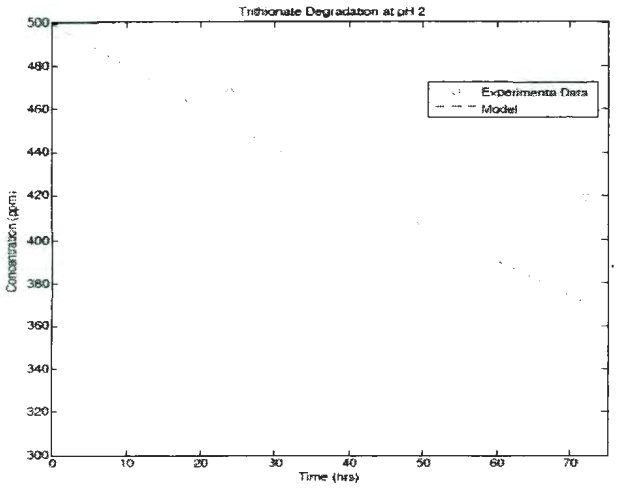


Figure 11. Comparison between predicted values and experimental data for trithionate at pH 2

Due to the lack of information available in the literature at different temperatures, the Arrhenius plot for trithionate includes only data from Meyer and Ospina (1982) and current experimental data (Figure 12). The results for the simulations are presented in Figure 13.

Table 7. Data for Arrhenius plot for Trithionate

Author	pH	Temp (°C)	K ($x10^3$)	N
Meyer and Ospina, 1982	4	20	3.1	1
Current Experiment	4	30	4.1	1

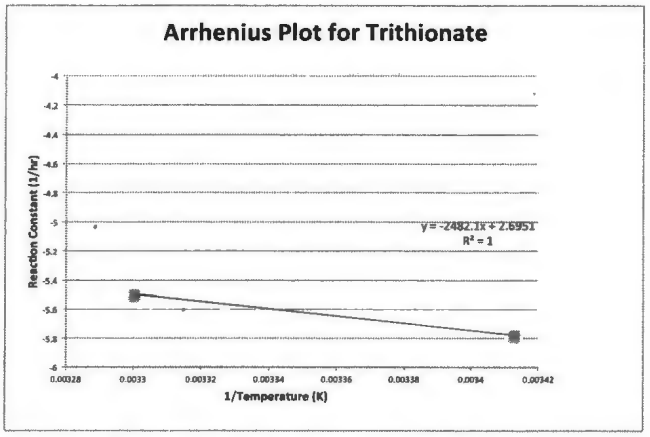


Figure 12. Arrhenius plot for trithionate

Energy of activation for trithionate in the pH range from 2 to 9 and a temperature range of 20 to 30℃ is 20.6 KJ and an Arrhenius constant of 14.8. Substituting those values into Equation 3, the parity plots shows in Figure 12 are constructed.

$$K = A_o e^{\frac{-Ea}{R*T}} \quad (3)$$

Parity plots show that the model fits the experimental data over the range of pH and temperature. However, at pH 9 the fit is not strong. Additional work (not shown) with data at higher pH shows that strong alkaline solutions enhance trithionate reaction so the use of Equation 3 with the values obtained in the experiment above pH 9 is not recommended. This also reflects earlier observations in the data shown in the van't Hoff plot in Figure 10, suggesting further work at higher pH is warranted. The parity plot at pH 4 includes the data from Meyer and Ospina (1982), who reported experimental results over 510 hours; that the proposed equation extends well to this long reaction time supports the validity of the model.

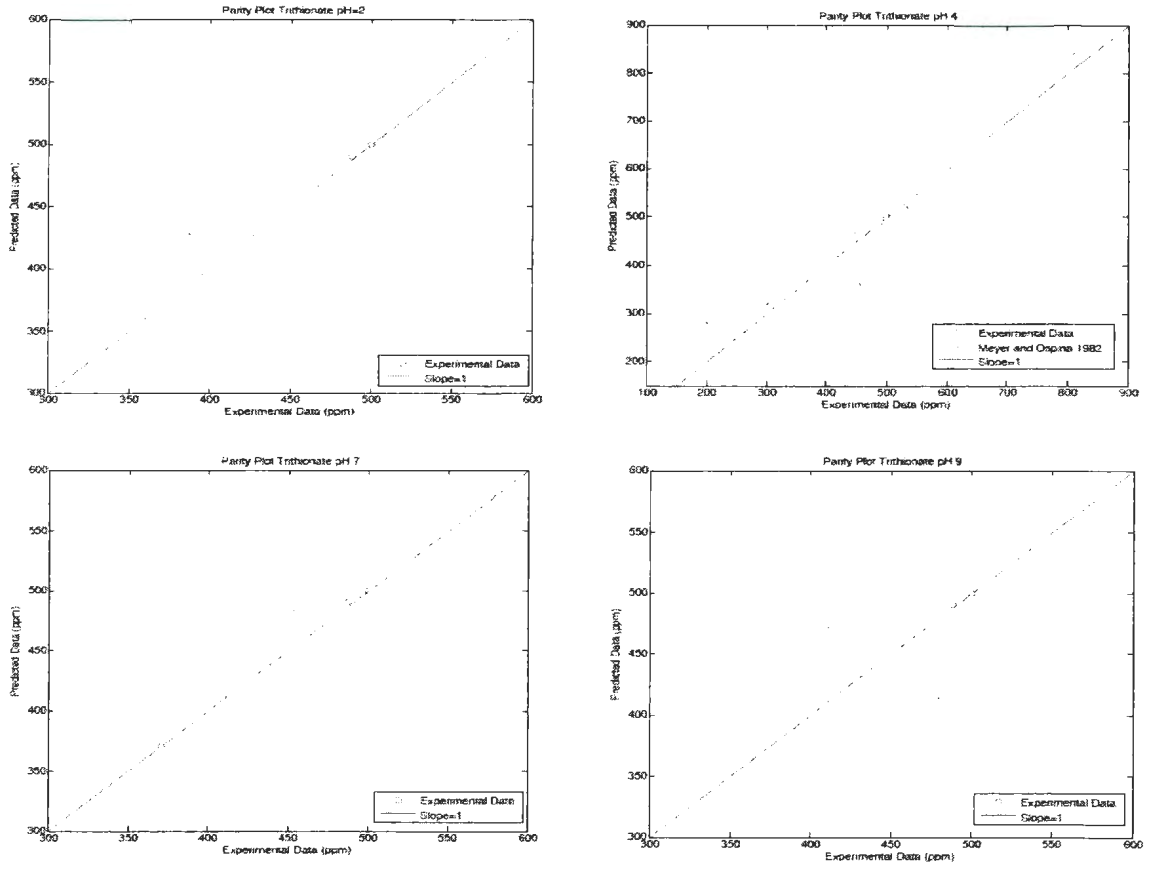
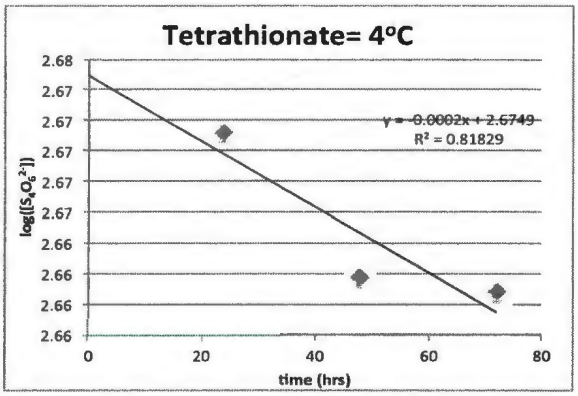


Figure 13. Parity plots for Trithionate

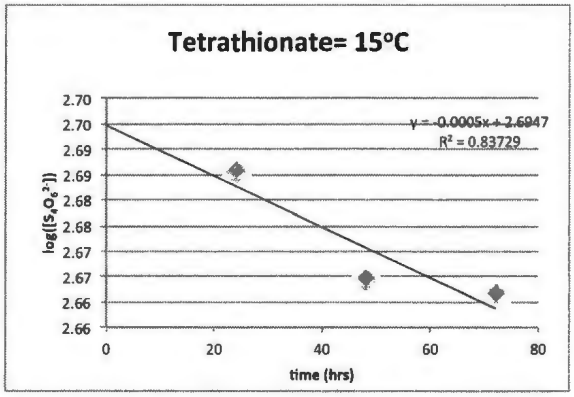
The study shows that trithionate plays an important role as the link between species reactivity along the different pH conditions of the solution, especially at temperatures around 30°C. Unlike thiosulfate, there was no sulfur or hydrogen sulfide evident during the experiments. The species we measured were proposed by Ahern *et al.* (2007), with the addition of tetrathionate as intermediate in the reaction, and should react to generate either thiosulfate or sulfate. An important observation is that unlike thiosulfate or tetrathionate the reaction rate for trithionate appears to be independent of pH, at neutral to acidic conditions.

3.4.3 Tetrathionate Results

Van't Hoff plots indicate tetrathionate decomposition is a first-order reaction in the temperature range between 4 and 30°C. Tetrathionate was reactive only in alkaline conditions (pH 9) in our experiments. Other authors, such as Varga and Horvath (2007) and Rolia and Tan (1985), also found tetrathionate to be reactive in alkaline conditions (pH 10.8 and pH 12, respectively), both proposing the same reaction order of one.



a)



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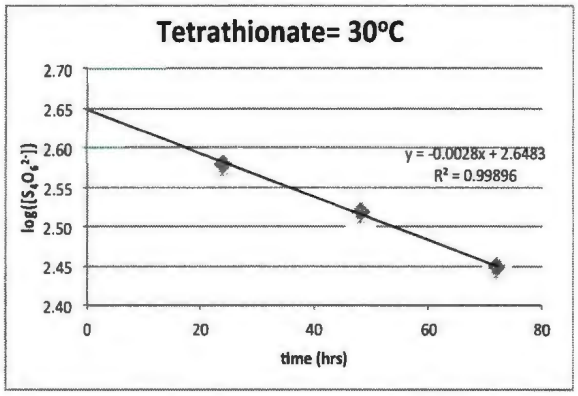

c)

Figure 14.Van't Hoff plots for Tetrathionate

The optimization routine used both our experimental data and Varga and Horvath (2007) data. Similar to thiosulfate, the reaction constant K is obtained by multiplying

K'bythe [OH^-] concentration in mol/L.The reaction constant increased with temperature as expected and the data from Varga and Horvath (2007) increased the pH range to 10.8. The Arrhenius plot for thiosulfate is shown in Figure 15.

Table 8. Tetrathionate optimization results

Reference	pH	Temp	K($x10^{-2}$)	n
Current Experiment	9	4	1.3	1
Current Experiment	9	15	1.3	1
Current Experiment	9	30	8.7	1
Varga and Horvath, 2007	10.8	25	7.29	1

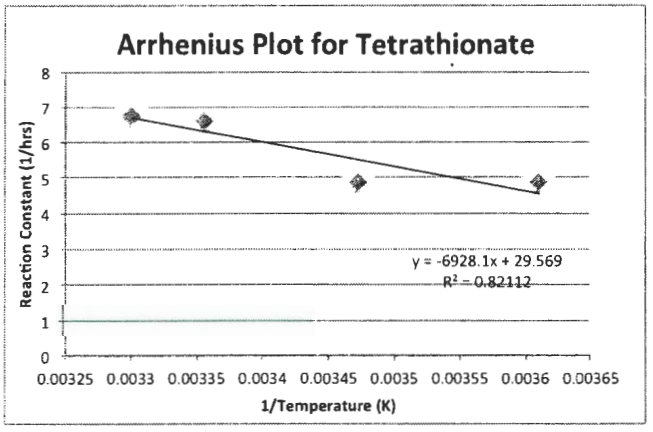

Figure 15. Arrhenius plot for tetrathionate

The activation energy for tetrathionate over a temperature range of 4 to 30℃ and pH from 9 to 10.8 is 57.6 kJ and the Arrhenius constant is $7.4x10^{12}$. The model predictions and experimental data are compared in Figure 16.

$$\frac{\delta[S_4O_6^{2-}]}{\delta t} = A_0 e^{\frac{-Ea}{RT}}[OH^-][S_4O_6^{2-}] \quad (4)$$

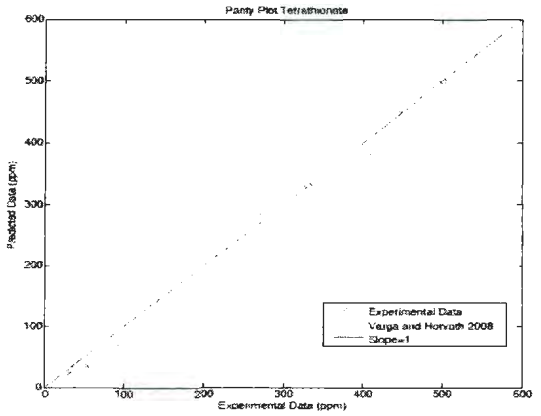

Figure 16. Parity Plot for Tetrathionate

The parity plot shows that the model predictions are very close to the experimental data up to 72 hours and Varga and Horvath (2007) data for 7 hours. The reaction rate equation includes temperature and pH dependency. Rolia and Tan (1985) studied tetrathionate reaction at pH 12, however, the data did not fit equation 4, indicating that the kinetics at that pH could be different than the kinetics studied here.

3.5 Reaction pathways

Experiments show that thiosalts species will be reactive depending on pH and temperature. For example, thiosulfate will react at acidic conditions (pH~2) while tetrathionate will react at alkaline conditions (pH~9). Trithionate is the only species in this study that shows reactivity among different pH values, but only at 30°C.

In the thiosulfate experiments, the species present in solution were the ones expected according to the proposed reaction mechanisms in Table 1 except for hydrogen sulfide, which was detected by its characteristic odor but was not quantified. Also, the generation of elemental sulfur was not quantified but analyzed by DSC and the yellow grains precipitated during the reaction were confirmed to be sulfur. It is possible that sulfite (as suggested by Xu and Schoonen 1995) could be present in solution at under-

saturated conditions of oxygen, however, this compounds was not analyzed in the lab. The reaction pathway proposed in Figure 18 is based only on the species detected in the lab, but they are in good agreement with that proposed by Mizoguchi*et al.*(1976) and with the stable species shown in the Pourbaix diagram shown in Figure 17. The presence of trithionate is proposed to be from tetrathionate; however, this was not experimentally verified.

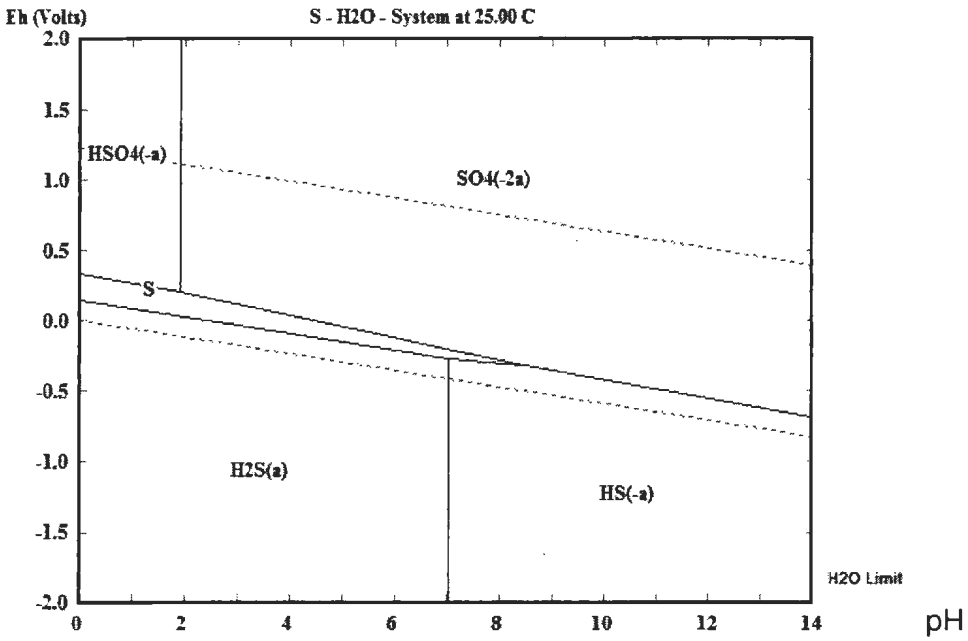

Figure 17.Pourbaix Diagram for S-H_2O system (Done in HSC)

According to the reactions proposed in the literature, tetrathionate is the only species out of the three studied that does not react directly to form sulfate. Therefore, its reaction must go to either trithionate or thiosulfate before completing its oxidation. This condition is important, as further reactivity will depend on the solution conditions. In our experiments, tetrathionate was only reactive at pH around 9 and the observed products of its reaction were thiosulfate and trithionate with traces of sulfate. Equilibrium results are complementary to the studies done in the lab, and in this case, because of

significant amounts of thiosulfate and trithionate detected experimentally, indicate that the experimental reactions are not at equilibrium.

Since sulfate dominates the results of the HSC equilibrium modeling, sulfate was removed as a potential product for the reaction of tetrathionate to better reflect the experimental results. The resulting Pourbaix diagram for the S-H_2O system (Figure 18) shows that thiosulfate is a stable species at high pH, while at low pH tetrathionate seems to be stable. This behavior is consistent with the experimental results gathered here as tetrathionate was only reactive at pH 9 and thiosulfate was reactive at pH 2. Since the experimental data also includes trithionate, trithionate is likely an intermediate during the reaction of tetrathionate at high pH. Though it seems that no sulfur or H_2S was produced in the tetrathionate experiments; they may have formed in very small amounts, and their absence is not inconsistent with the Pourbaix diagram as reflects a system at equilibrium, which is an unlikely state for these experiments over the time scales of the study.

The two main products of the trithionate reaction according to our experimental data are sulfate and thiosulfate with small amounts of tetrathionate; this is in agreement with the reaction proposed by Ahern (2007). A key trithionate characteristic is its reactivity over the pH range of the study, hence the final product of it oxidation will depend on the pH of the solution. In other words, at acidic conditions, the sulfate concentrations are expected to be higher, while in alkaline solutions, the concentration of thiosulfate will be dominant among the products.

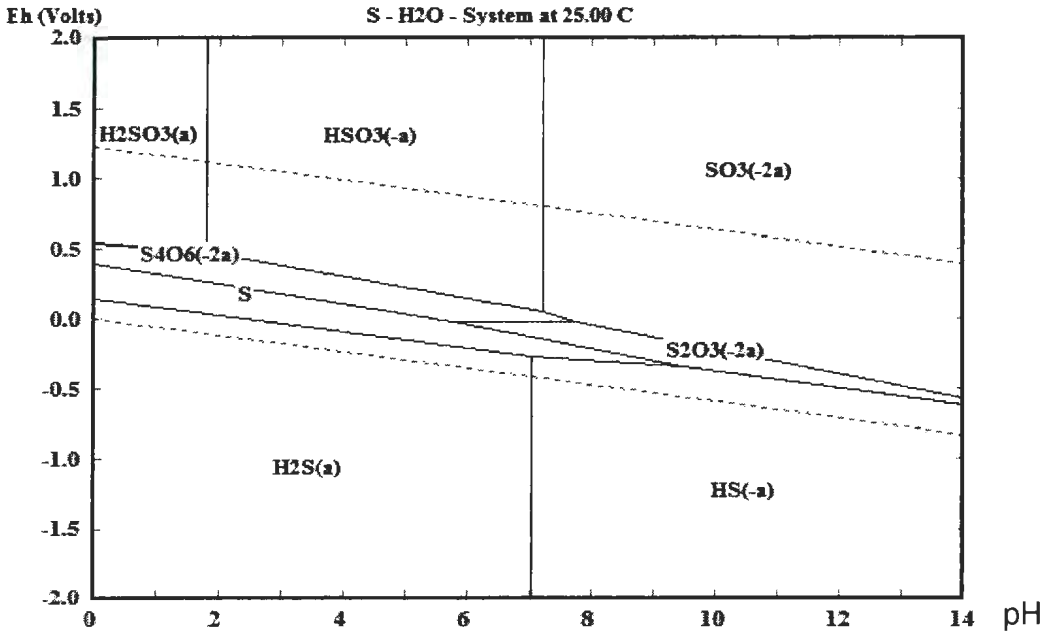

Figure 18.Pourbaix Diagram for S-H_2O system removing sulfate as a species in solution

As shown in Table 1, there are several different pathways proposed for thiosalt reactions at different pH and temperature conditions. The following global reaction equations are reported by different authors and selected as they represent most of the species followed in the lab:

Table 9. Proposed reactions for thiosalt oxidation

Thiosalt	**Reaction**	**Reference:**
Trithionate	$S_3O_6^{2-} + H_2O \rightarrow S_2O_3^{2-} + SO_4^{2-} + 2H^+$	Ahern *et al.* 2007
Thiosulfate	$5S_2O_3^{2-} + 6H^+ \rightarrow 2S_4O_6^{2-} + 2S^o + 3H_2O$	Mizoguchi*et al.* 1976
Tetrathionate	$4S_4O_6^{2-} + 6OH^- \rightarrow 5S_2O_3^{2-} + 2S_3O_6^{2-} + 3H_2O$	Varga and Horvath 2008

From the information gathered in lab and the reactions proposed by different authors, a global pathway for thiosalts reactions using the species that we were able to detect in the lab is presented in Figure 19.

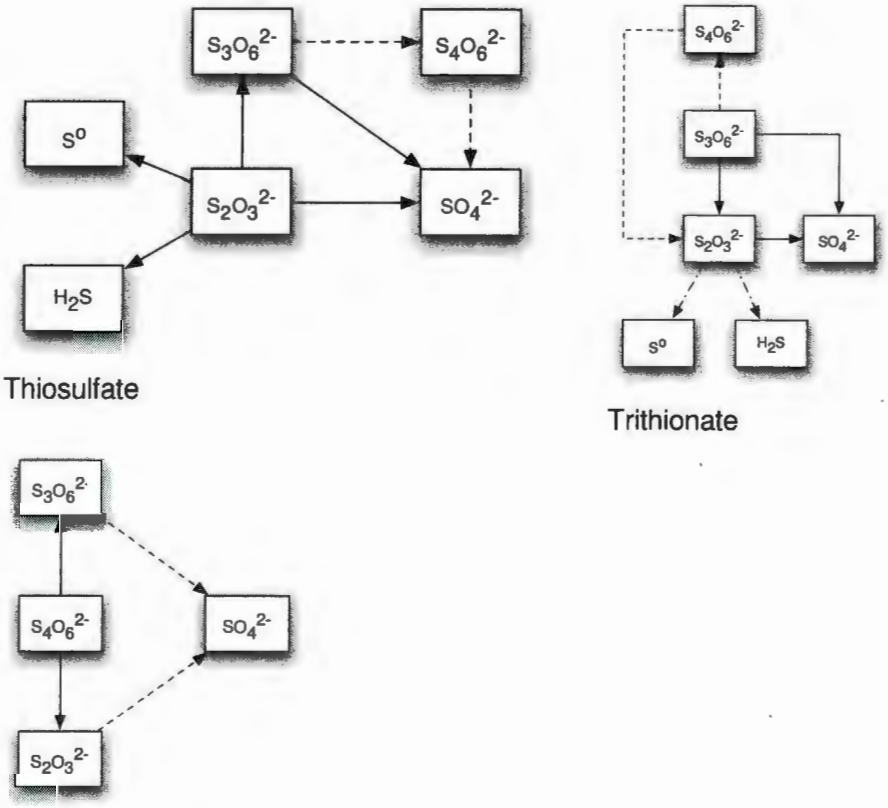

Figure 19. Global reaction pathways proposed from the species detected in lab experiments

The pathways presented in Figure 19 are called global as they do not identify all of the intermediates present in the reaction but in this case, only the sulfur species of interest. The dotted lines show pathways that are possible as reported in other studies and that

the experimental data show are either very slow or fast in the timeframe of the experiment.

4. Conclusions

Rate equations under different pH and temperature conditions and transformation pathways were developed for the three main thiosalts species. For the trithionate and tetrathionate kinetic equations, an adjustment factor that considers the proton concentration (pH) was included. Trithionate is the only thiosalt species in this study that was able to react under both acidic and alkaline conditions, which points to a special role for trithionate in the oxidation pathways. Our results are consistent with observations that thiosalt reactivity is highly dependent on temperature, but also illustrates the importance of pH in the reactivity of these species. Thus any studies involving thiosalts must include pH as a key factor.

From the information gathered in the experiments, simulations in HSC and reactions previously proposed, we have proposed a few general reaction pathways in the oxidation of thiosalts. These pathways will be helpful in thiosalt management in tailing ponds. Knowledge of the pathways combined with the kinetic equations, can be implemented in the development of refined pond and treatment models to yield a more detailed and accurate picture of the thiosalt transformations and fate, and to develop the most effective and economical treatment process. Though beyond the scope of this work, the role of reagents and catalysts used in thiosalt treatment must also be considered in the development of robust models, particularly in light of the complexity of thiosalts chemistry.Thiosalt speciation is highly dependent on temperature and pH; thus any studies involving thiosalts must include both factors. Future studies will be focused on the effect of reagents in the kinetics of the different species and their effect on the general reaction pathway.

5. Acknowledgements

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Chapter 3

The effect of temperature and pH on speciation of thiosalt mixtures

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Abstract

Tailing ponds management is critical both in terms of reducing the environmental impact of mining operations and reducing cost associated with inefficient treatment/disposal. Thiosalt species present in mining effluents, such as thiosulfate, trithionate and tetrathionate, have been identified as precursors of acid mine drainage (AMD) generation and the subsequent pH depression in the discharge effluent. Current treatment technologies and pond management strategies do not consider the speciation of thiosalts and its effects on treatment efficiency and AMD generation. Previous studies have followed the kinetics of each individual thiosalt species, however, the interactions between species impact these reaction pathways and hence the rates. In this study, the reaction rates from thiosalt mixtures of thiosulfate, trithionate and tetrathionate are analyzed under pond conditions (pH range of 2 to 9 and temperatures between 4 and 30°C). Following a decoupling approach and using equilibrium prediction as a tool, the reaction rates for each species as well as potential global reaction pathways for the species are proposed.

1. Introduction

The presence of thiosalts in effluent discharge is the result of partial oxidation of sulfide minerals during the mining process (Rolia and Tan, 1985). Studies by Schwartz *et al.* (2006) and Yaschyhyn (2006) concluded that thiosalts are not acutely toxic to species such as rainbow trout and Daphnia Magna. Nevertheless, ecosystemscan be affected by the potential pH depression generated by thiosalt oxidation; these sulfur intermediates have already been identified as precursors of acid mine drainage (AMD) (Druschell*et al.*, 2004; Johnson, 2003).

Thiosulfate, trithionate and tetrathionate are the stable species under typical pond conditions (Wasserlauf and Dutrizac, 1982) and the reaction rates for individual thiosalts at specific conditions have been studied before(Ahern, Druschell, Varga, Xu). Nevertheless, the complexity of thiosalts reactions is compounded by the variety of different factors that affect them. For example, Wasserlauf and Dutrizac (1982) identified the importance of thiosalt speciation and its effect on the different reactions that could occur,and also presented the interactions that each species could have in the mixture:

$$S_nO_6^{2-} + S_2O_3^{2-} \overset{H^+/OH^-}{\longleftrightarrow} S_{n+1}O_6^{2-} + SO_3^{2-} \qquad (1)$$

Varga and Horvath (2007) and Meyer and Ospina (1982) proposed similar reactions, however, they also noted the presence of thiosulfate as catalyst for tetrathionate degradation at neutral pH

$$2S_4O_6^{2-} \overset{S_2O_3^{2-}}{\longleftrightarrow} S_5O_6^{2-} + S_3O_6^{2-} \qquad (2)$$

Understanding thiosalt reactivity in the pond is critical as water management and treatment will depend on it. Past experiments in our lab (Vongporm, 2008) identified the conditions at which each thiosalt species is reactive, as shown in Figure 1. These

conditions are in agreement with the general trends identified by Wasserlauf and Dutrizac (1982) that polythionates are unstable in alkaline conditions while stable in mild to strong acid solutions. Nevertheless, as noted in reactions 1 and 2, the behavior of thiosalts in a mixture could be different than the behavior of the species on their own as some species, especially thiosulfate, can act as catalysts in polythionates degradation.

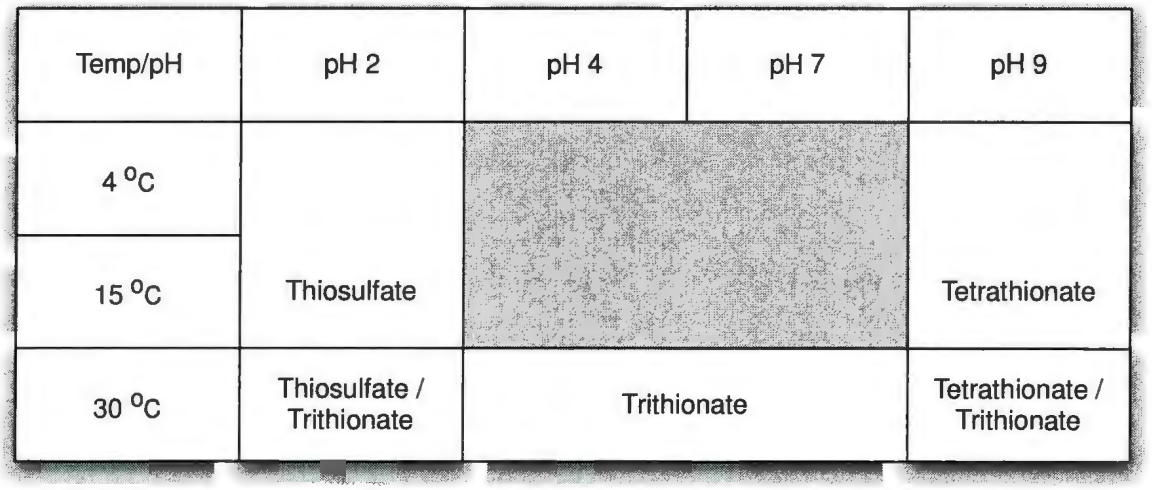


Figure 1. Reactive conditions for each thiosalts

In previous studies,we have proposed reaction rate equations for each species as a function of temperature and pH (Miranda *et al.* 2012). These equations serve as starting pointsin determining the behavior of the species in mixtures. Thiosalt reactivity is influenced byreagents or catalysts, pH and temperature (Wasserlauf and Dutrizac, 1982).The lack of established reaction rate data for thiosalt species and good speciation predictions forspecific ponds has typically resulted in over-treatment by oxidation of thiosalts in effluent, and higher than should be necessary demands in neutralization of the effluent.The environmental benefits of the treatment could be offset by the increased costs of excessive chemical use and the impact of sludge generation. To better design and develop effective thiosalt management systems, reaction rates accounting for speciation are required. These rate equations should include the effect of pH and temperature as well as the presence of the other thiosalt species. The understanding of reaction rates in mixtures could impact treatment efficiency by enhancing thiosalts

oxidation hence, reducing pH depression and reducing cost and chemical use in the pond.

The objective of this paper is to analyze the behavior of thiosalts mixtures at various pH values and to use the data to develop appropriate reaction rates equations for these mixed systems. These equations, in addition to equilibrium predictions, could provide information needed to determine global reaction pathways. To determine relative reaction rates, batch experiments were performed under pH and temperature conditions typical of the effluent ponds. The specific sampling protocols are outlined in the experimental method sections. The analytical advantages and protocol using capillary electrophoresis are explained in the analytical method section. Finally, the approach taken to analyze the kinetic data and additional simulations done in HSC to obtain equilibrium information are explained.

2. Research Strategy and Experimental Methods

2. 1 Batch Studies

Batch studies were conducted with the three main thiosalts species under different conditions of pH and temperature to development a global reaction rate. Three thiosalts were studied: thiosulfate, trithionate and tetrathionate. Sodium thiosulfate pentahydrate from Merck and potassium tetrathionate from Sigma-Aldrich were used during the experiments. Trithionate is not commercially available and was synthesized using a modified Kelly and Wood (1994) method.

The pH of the solutions was maintained using buffer solutions; pH 2 did not use a buffer, but diluted acid, but for ease, the term "buffer" will be applied to all solutions used to control pH. The solution at pH 2 was achieved using glacial acetic acid diluted until the pH read with a calibrated pH meter was 2; pH 4 used 50 mM ammonium acetate/acetic acid; pH 7 the buffer used 50 mM ammonium dihydrogenphosphate/ ammonium hydrogenphosphate and for pH 9 a 50 mM ammonium acetate/ammonium hydroxide buffer was used. In all cases, the mixtures of acid and conjugate base to

make the buffers were adjusted to the appropriate pH measure with a calibrated pH meter using the appropriate acid or base for the system.

Batch study experiments (Table 1)used mixtures of thiosalt species prepared by dissolving the selected amount(s) of thiosalt species in 100 mL of buffer solution. The resulting solutionswere transferred to 250-mL volumetric flasks, sealed with stoppers and agitated at the temperature of study. 1.5-mL aliquots were taken at specific times and filtered using a 0.2 µm nylon syringe filter. The sampling protocol (after Vongporm, 2008) was as follows; filter sample and immediately freeze in liquid nitrogen and store at -80°C until analysis, on the day samples are to be analyzed, frozen samples are transferred from the ultralow freezer (-80°C) to a regular freezer (-4°C) and then only allowed to thaw for 10 minutes before analysis.

As previously indicated, the experimental conditions reflected the effluent treatment/pond conditions as outlined in Table 1.

Table 1. Experimental conditions

Variables	Levels
Thiosalts in the Mixture	Thiosulfate, Trithionate, Tetrathionate
Temperature (°C)	30
pH	2, 4, 7, 9
Concentration (mg/L)	500
Time	0 to 72 hours

2.2 Analytical Method

Thiosalts were quantified using capillary electrophoresis (CE) (Agilent 1602) with UV detection. CE was chosen over ion exchange chromatography for a number of reasons: it is a rapid analysis method (5 minutes for most common thiosalts (Pobozy et al, 2002)), has very good anion separation efficiency, low operational cost and consumes small sample volumes (Haddad, 1997; Motellier and Descostes, 2001). A 50 µm inner diameter base fused silica capillary (Microsolv Technology Corporation), 48.5 cm total length and 40 cm effective length was used in all analyses. The capillary is loaded in a cassette and the temperature of the equipment is set at 23°C during experiments. The background electrolyte (BGE) used was waspyromellitic acid (chromophore), hexamethonium bromide (EOF modifier) and Triethanolamine (for pH adjustment) and filtered with a 0.2 µm nylon filter before use. The sample was placed on a 1-ml polypropylene vial with polyurethane snap cap. The operational procedure for the CE was to flush capillary with sodium hydroxide 1 M solution for 15 min followed byBGE for 10 min; inject samplehydrodynamically with a pressure of 50 mbar for 10 seconds;carry out separation by applying a voltage of 30 kV in negative polarity mode. The detection wavelengthswere 214 nm for thiosulfate and tetrathionate, 194 nm for trithionate.

2.3 Equilibrium Analysis and Determination of Reaction Rates.

Equilibrium analysis is a useful tool to identify reactants or products that could participate in thereaction. Reaction equilibrium predictions for the thiosalts mixtures were calculated by the Gibbs free energy minimization approach using the HSC Chemistry software V7.0from Outotec. Thiosalts reactivity is governed by pH and temperature for the range of pond conditions studied (Vongporm, 2008). As such, in these calculations the pH of the solution to be studied was input accordingly and the equilibrium position analyzed from 0 to 30°C.

Reactions rates were derived using the method from a previous study (Miranda et al., 2012)based on the initial rate method. In the mixtures, the reactions are more complex

and species consumed in single species experiments may be consumed and/or generated in mixtures. To account for this, we have combined the reaction rate equations derived from single species experiments and added an additional term to account for additional reactions. It should be noted, this is a global reaction rate equation and does not reflect the specific reactions occurring in the mixture but rather species behavior in solution:

$$\frac{d[C]}{dt} = -K_r[C]^n + K_p[C]^m \quad (3)$$

where K_r is the reaction constant for the consumption and K_p is the reaction constant for the generation of thiosalt, n and m are the orders, C is thiosalt concentration and t is time. Thiosalt reactivity varies at different temperature and pH conditions, and in this case, the species present in the mixture. As such, values for the two variables (K and n) of Equation 3 should be estimated by fitting measured data from experiments performed under different combinations of these parameters. This fitting problem is over-determined, and thus vastly different values of K and n can provide equally good fits to the experimental data. To obtain a meaningful physical result, the optimization has to be constrained to thermodynamically realistic values. Our approach used a two-step sequential optimization. The first step was an exhaustive search of K and n values over a discrete range of values (n had a range between 0 and 3 and K from 0 to 1). We used an explicit Runge-Kutta approach (in Matlab Student Version 2011a) to numerically solve Equation 1 for each (K,n) pair, and each set of initial conditions and pH values. The numerical solutions of the ordinary differential equation(ODE) were then compared to the corresponding experimental data to see which values of K and n provided the smallest least-squares error. In the second step, we used the Matlab constrained minimization method *fmincon* to refine the estimates of K and n, beginning from the best values found in step 1. In both steps the simulations were done only under conditions where thiosalts are reactive.

3. Results

The first part of this sectionoutlines the results of the equilibrium analysis of the mixtures followed by the experimental results. A material balance for sulfur and oxygen add additional background information for the potential reaction pathways. In the last part, the reaction rates for the main sulfur species are proposed. The sulfur speciesmeasured during the analytical procedure were thiosulfate, trithionate, tetrathionate and sulfate.

3.1 HSC Equilibrium Simulation

The equilibrium analysis based on Gibbs Free Energy minimization predicts final product distribution in the sample over the range of pH and temperatures used in the experiments. The product distribution at equilibrium provides a reference for the kinetic studies in terms of reaction progress. The initial concentrations in the simulation were set at 500 mg/L for each thiosalt. The simulation was run for all pH values over the range of interest, as previous experiments have shown than at least trithionate will be reactive over that pH range. Solution pH was maintained by adding buffer compounds in the simulations, and in all cases the final pH was within 0.5 units of the initial pH.The simulations were done with oxygen in excess in solution. The results of the simulation are presented in Table 2.

Table 2 Simulation results for thiosalt mixtures.

	pH 2 Temp 4-30℃	**pH 4 Temp 4-30℃**	**pH 7**			**pH 9**		
			4℃	**15℃**	**30℃**	**4℃**	**15℃**	**30℃**
Thiosalt Mixture*	S^0 30% SO_4^{2-} 70%	S^0 30% SO_4^{2-} 70%	HS^- 45% H_2S 55%	HS^- 54% H_2S 46%	HS^- 63% H_2S 37%	HS^- 78% H_2S 22%	HS^- 72% H_2S 28%	HS^- 65% H_2S 35%

* 500 mg/L of each of the following thiosalts: thiosulfate, trithionate and thiosulfate

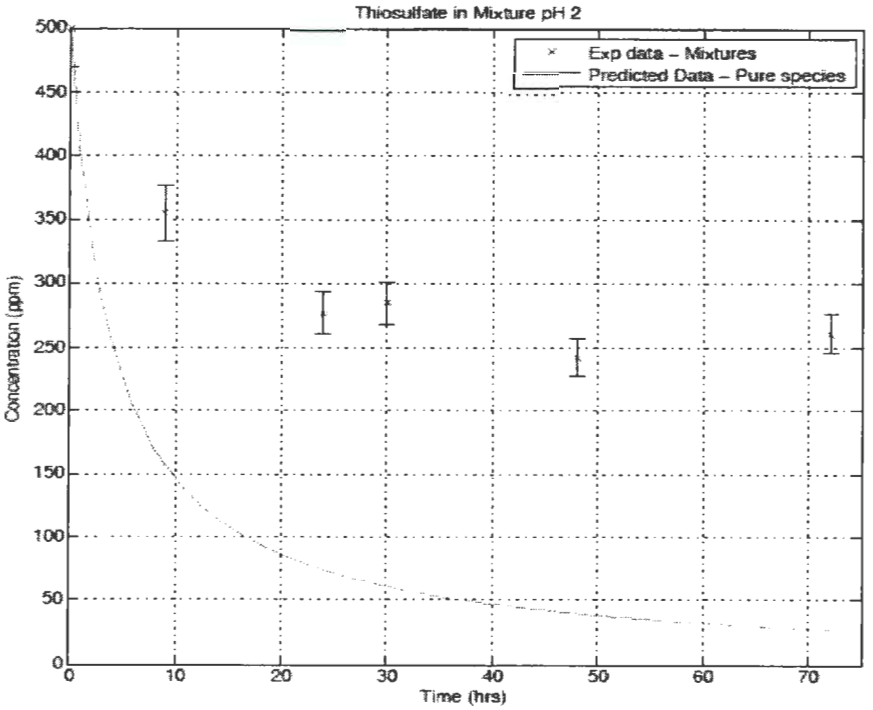
The species distribution in equilibrium for a mixture of thiosulfate, trithionate and tetrathionate in the pH range of 2 to 4 is ~30% sulfur and ~70% sulfate. At neutral and alkaline pH, the equilibrium products were hydrogen sulfide (H_2S) and hydrosulfide (HS^-

), with distribution varying according to temperature (Table 2). Sulfate and elemental sulfur are known products of thiosalt oxidation; hydrogen sulfide is usually found in thiosulfate oxidation at low pH.

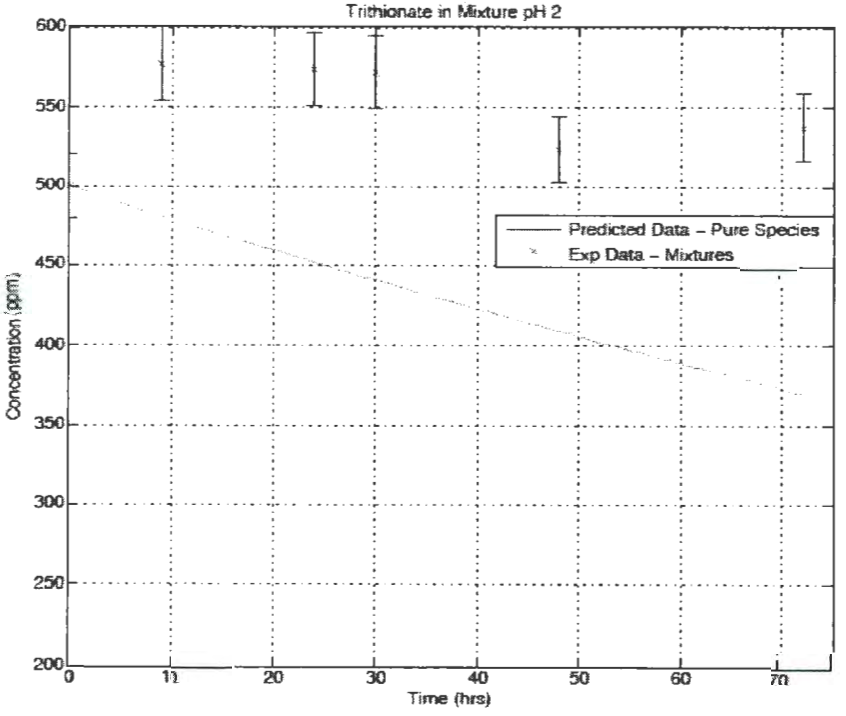
3.2 Experimental Results

Thiosalts in solution will have multiple reaction pathways (Varga and Horvath, 2007; Meyer and Ospina, 1982). The purpose of the experimental work was to identify the change in reaction rate and correlate the results obtained in a previous pure species analysis with the mixture results. Thiosalt reactivity in mixtures is expected to be similar to the results with individual species (i.e., thiosulfate will be reactive at pH 2, tetrathionate at pH 9 and trithionate in all the pH range). The degradation of each thiosalt in the mixtures at different pH is shown in Figures2 to 5.

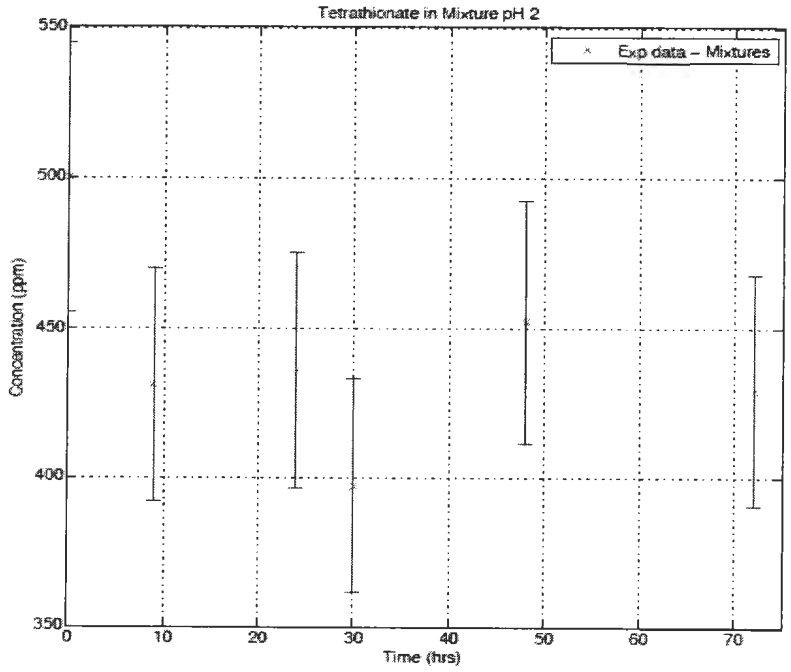
Thiosulfate is the most reactive of the thiosalts at pH 2 (Figure 2a), while trithionate and tetrathionate concentration do not change (within analytical experimental error). In the case of trithionate, it is likely that the degradation and accumulation rate is equal at these conditions, as this compound does show reactivity as a pure species. For tetrathionate, the pure species analysis showed no reactivity at pH 2, hence the change in concentration is attributed to experimental error (Figure 2c, error margin is magnified by the short concentration range of the figure). The sulfate concentration in solution also increases with time as a result of the thiosalt oxidation.Druschell (2002) reported a rearrangement of tetrathionate at low pH under very specific conditions, such as concentration above 5000 μM and at a temperature of 25℃, in which 13% of tetrathionate converted to trithionate in the first 90 min. However, those values are very close to the measurement error (9%) hence it is difficult to quantify if that same behavior is occurring in this experiments.


Thiosulfate in Mixture pH 2
Exp data – Mixtures
Predicted Data – Pure species
Concentration (ppm)
Time (hrs)
0
50
100
150
200
250
300
350
400
450
500
0
10
20
30
40
50
60
70

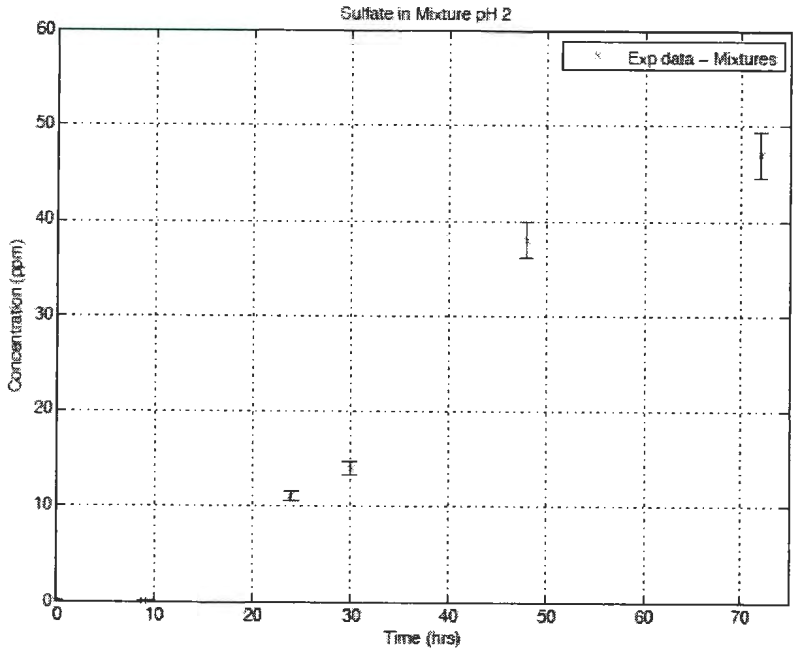
(a)


Trithionate in Mixture pH 2
Predicted Data – Pure Species
Exp Data – Mixtures
Concentration (ppm)
Time (hrs)
200
250
300
350
400
450
500
550
600
0
10
20
30
40
50
60
70

(b)



(c)

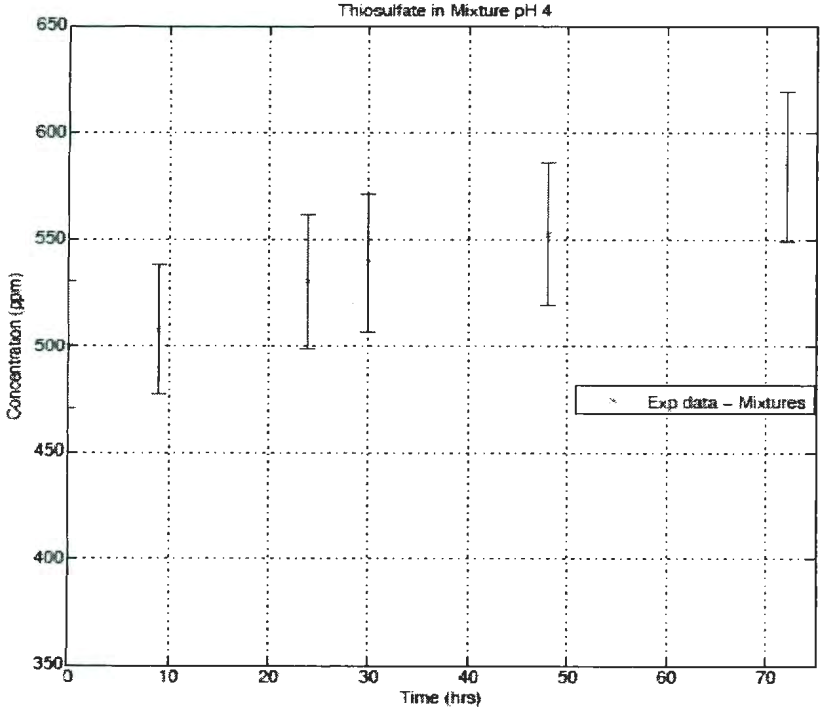


(d)

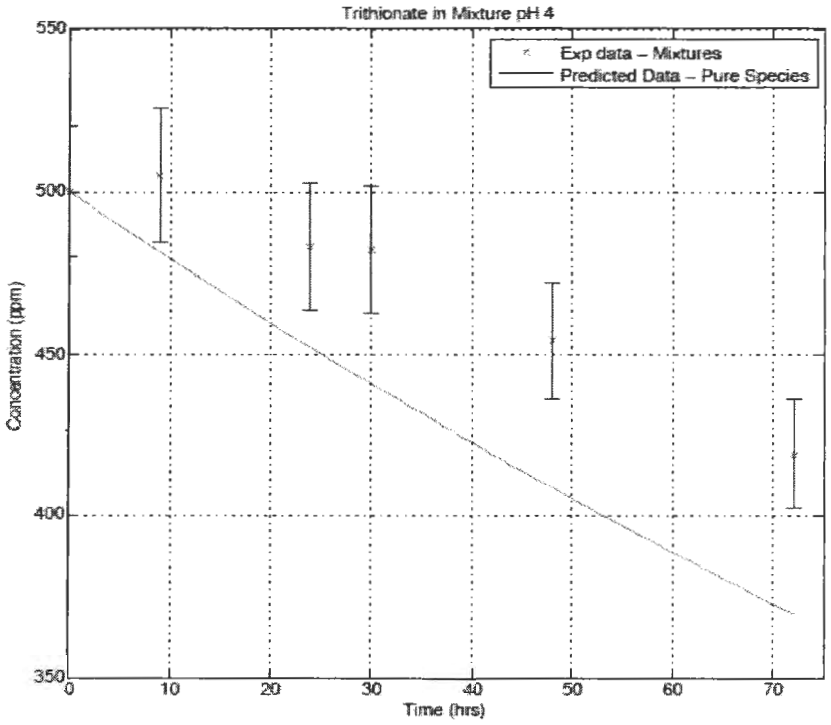
Figure 2 Sulfur species concentration in the mixture at pH 2

At pH 2, there is a small increaseof sulfate with time, while tetrathionate is seems to be somewhat unreactive after a relatively fast decrease to a concentration between ~400 and 450 mg/L. Trithionate is either unreactive or formation and consumption rates are approximately equal, and thiosulfate decreases fairly rapidly initially then change in concentration then appears to level off.

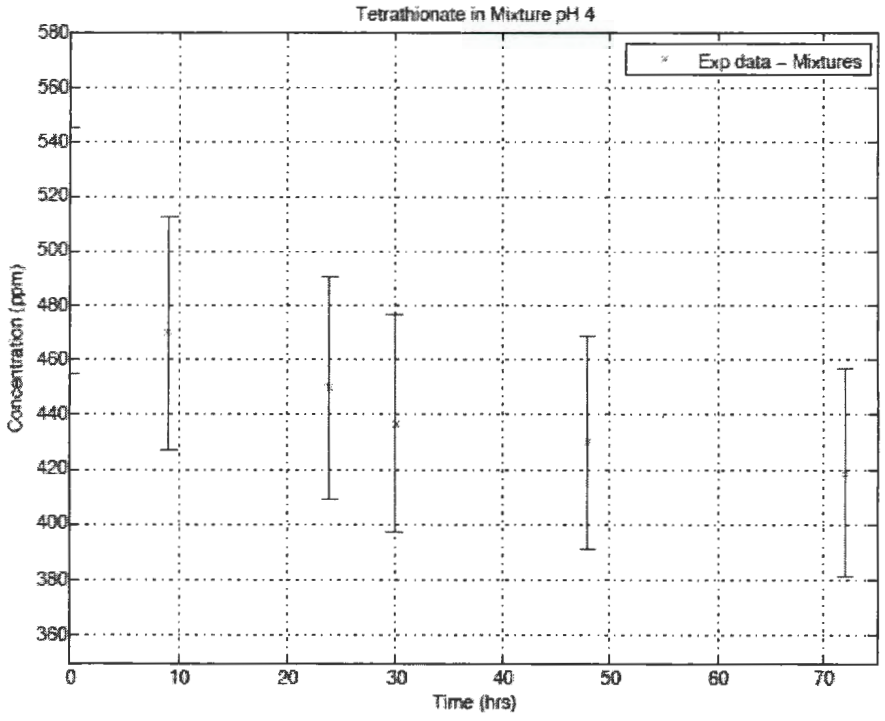
The behavior of mixtures at pH 4 (Figure 3) follows the expected trend based on previous experiments and equilibrium calculations. Thiosulfateand sulfate are generated at pH 4, and the generation of sulfate is slightly higher than at pH 2, but it is still very low in comparison with the sulfate concentrations predicted by the single species rate expression.



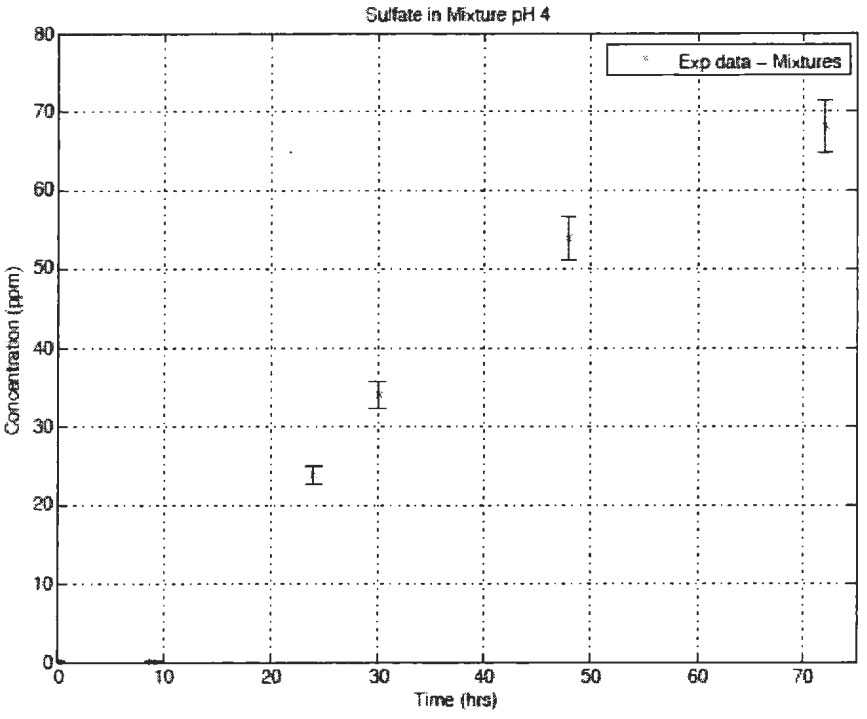
(a)


Trithionate in Mixture pH 4
Exp data – Mixtures
Predicted Data – Pure Species
Concentration (ppm)
Time (hrs)
550
500
450
400
350
0
10
20
30
40
50
60
70

(b)


Tetrathionate in Mixture pH 4
Exp data – Mixtures
Concentration (ppm)
Time (hrs)
580
560
540
520
500
480
460
440
420
400
380
360
0
10
20
30
40
50
60
70

(c)

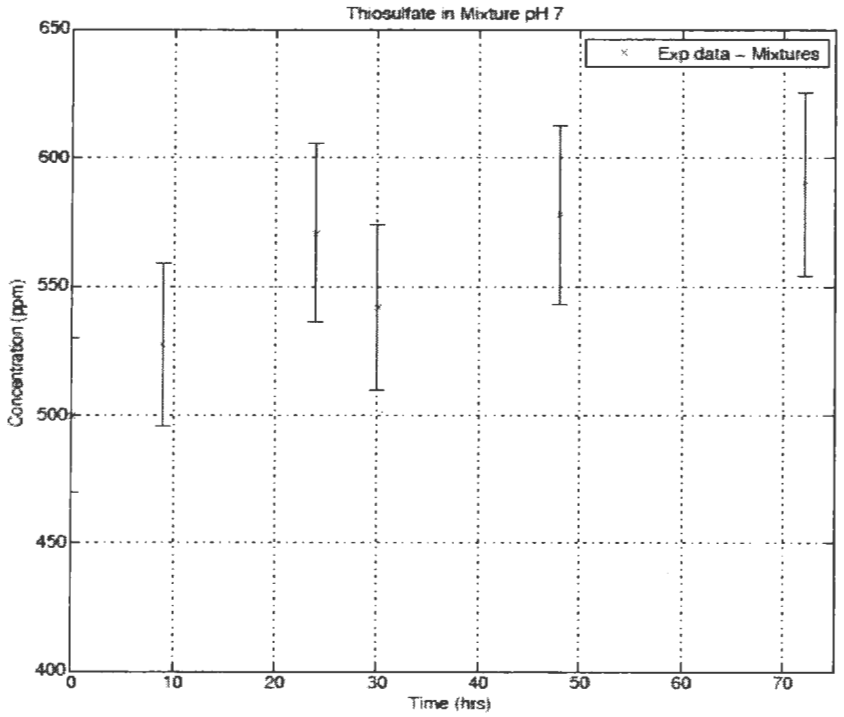


(d)

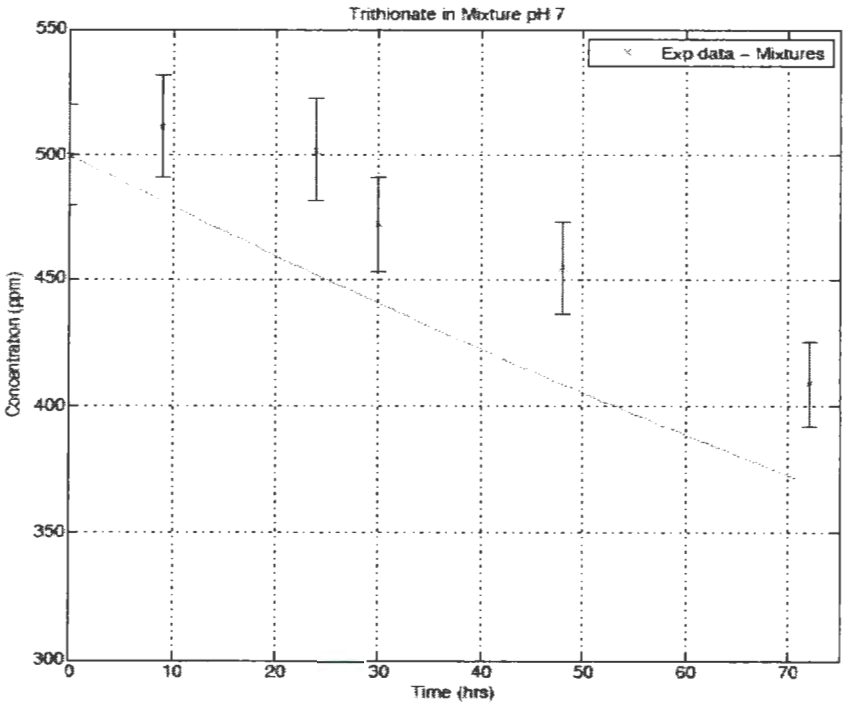
Figure 3.Sulfur species concentrationin the mixture at pH 4

At pH 4,therate of decrease for the trithionateconcentration in the mixture observed is slower than analogous experiments for the pure species. Also, there isgeneration of thiosulfate and sulfate; while tetrathionate concentrations do not change within the experimental error of the method therefore it is difficult to determine reactivity.

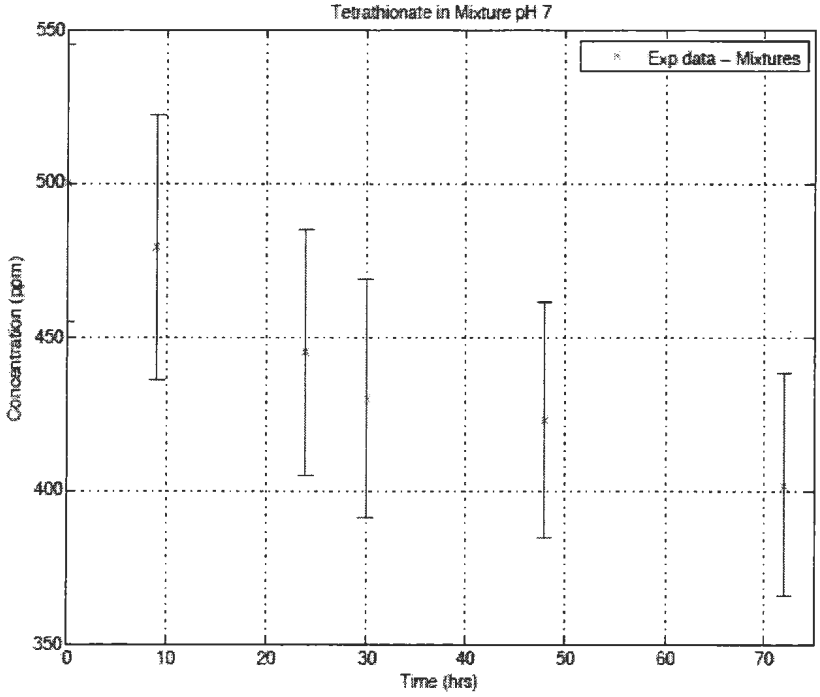
At pH 7 the concentration changes are very similar topH 4 values. For example, thiosulfate generation increases approx. 100 ppm or 1.8 mmol, while the combined sulfur percentage in trithionate and tetrathionate decreases approximately the same amount of mmoles. For sulfate, the increase is also in the range of 1%. This indicates that the reactions or distribution of species likely follow a similar reaction pathway at both conditions.


Thiosulfate in Mixture pH 7
Exp data – Mixtures
Concentration (ppm)
Time (hrs)
650
600
550
500
450
400
0
10
20
30
40
50
60
70

(a)


Trithionate in Mixture pH 7
Exp data – Mixtures
Concentration (ppm)
Time (hrs)
550
500
450
400
350
300
0
10
20
30
40
50
60
70

(b)



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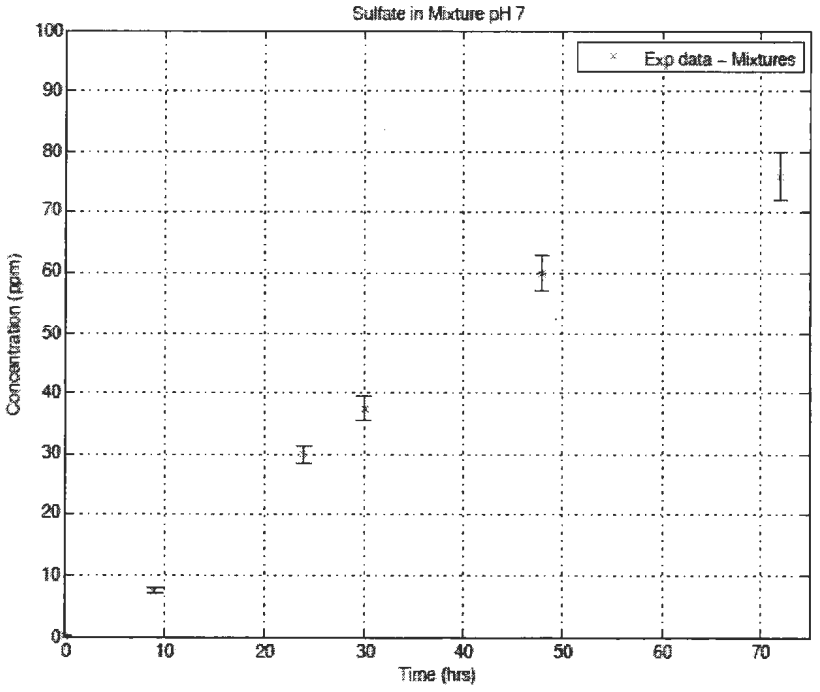
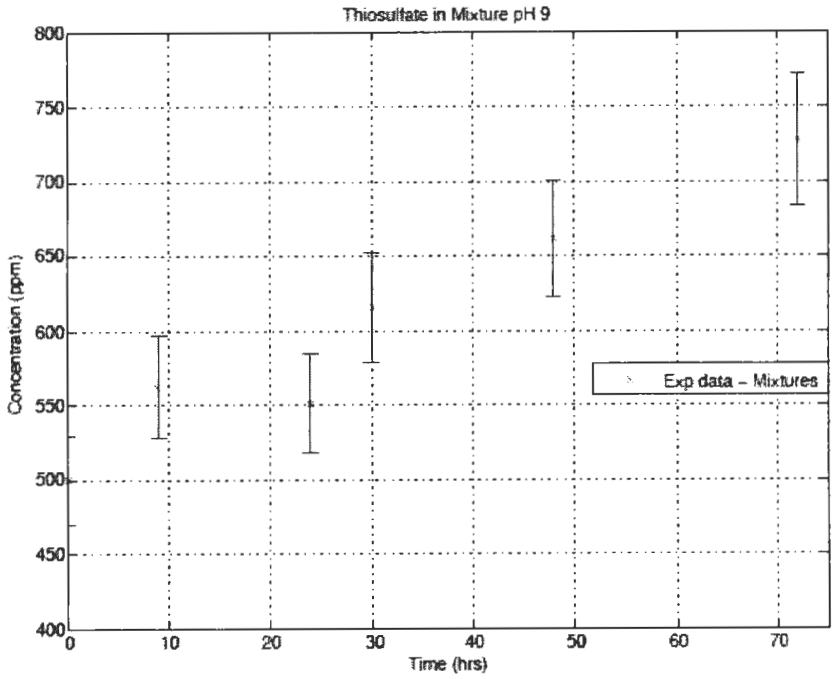


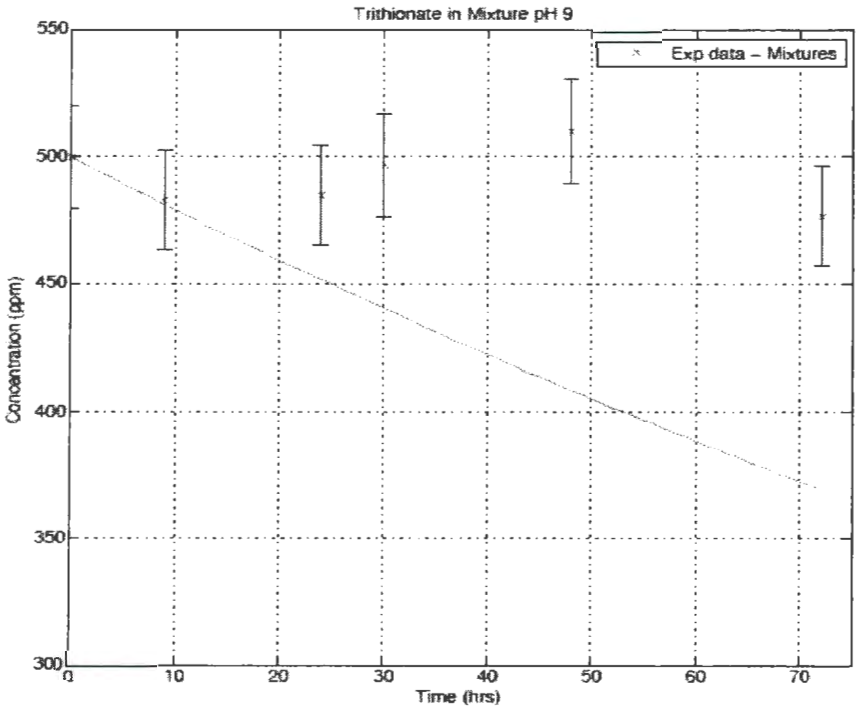
(d)

Figure 4.Sulfur species concentrationin the mixture at pH 7

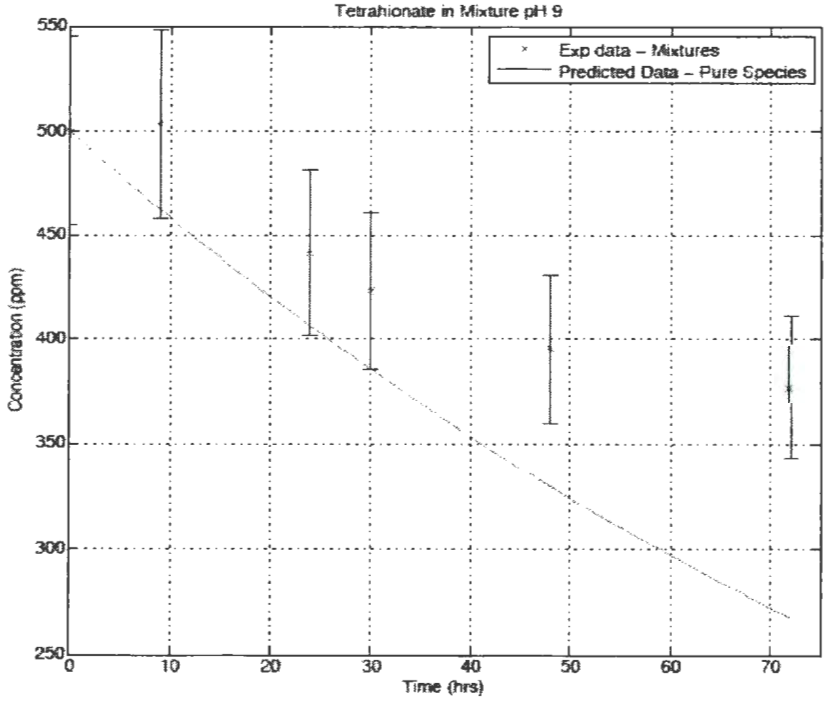
At pH 9, tetrathionate is most reactive while trithionate is marginally reactive(Figure 5d). As expected, there is a decrease in tetrathionate in solution (~10% of sulfur) and anincrease(~ 15% of sulfur) in thiosulfate. An interesting trend is that trithionate remains practically stable during the experiments (up to 72 hrs.), whereas in the single species experiments trithionate is reactive. Thus, the apparent stability could indicate that the generation and consumption of trithionate is in equilibrium in the mixtures (i.e., the generation and consumption rates areequal). As in the other conditions, the generation of sulfate is very limited.



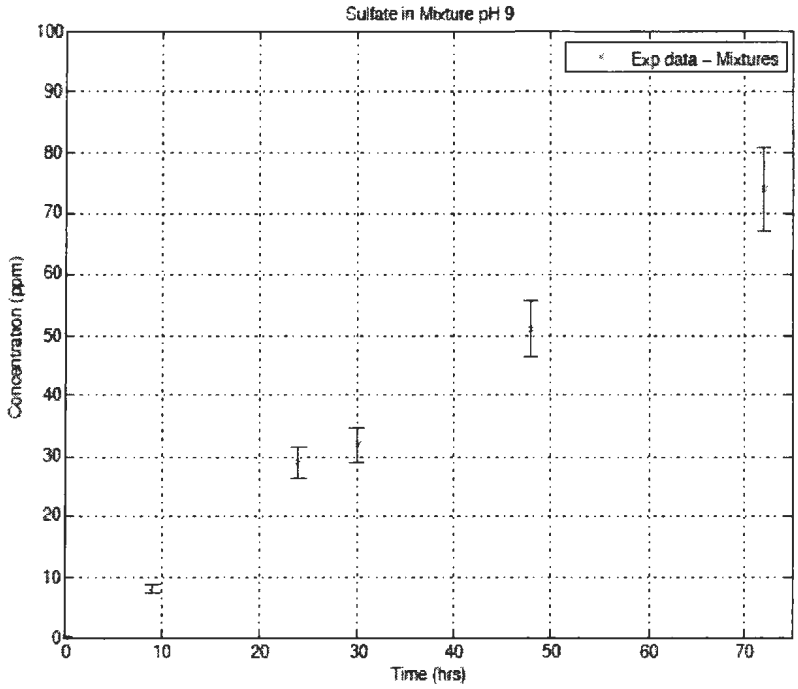
(a)


Trithionate in Mixture pH 9
Exp data – Mixtures
Concentration (ppm)
Time (hrs)
550
500
450
400
350
300
0
10
20
30
40
50
60
70

(b)


Tetrathionate in Mixture pH 9
Exp data – Mixtures
Predicted Data – Pure Species
Concentration (ppm)
Time (hrs)
550
500
450
400
350
300
250
0
10
20
30
40
50
60
70

(c)



(d)

Figure 5.Sulfur species concentrationin the mixture at pH 9

The experimental results in the pH range of 2 to 9 shows sulfate is not a major product in the mixtures for time scales of these experiments. At pH 2, the generation of trithionate is likely due to thiosulfate consumption. At pH 4 and 7, the opposite occurs, as thiosulfate is generated, likely through trithionate consumption. At pH 9, tetrathionate degradation generates thiosulfate possibly via trithionate.

Material balances can provide additional information to elucidate the global reaction pathways to develop the reaction rates in the mixtures. This information is presented in the following section.

3.3 Material Balance in Solution

The balance of sulfur and oxygen can be used to develop an understanding of the reaction pathways of sulfur, by showing how the sulfur is being distributed in the

different species. Table 3 shows a comparison between the initial amounts of sulfur and oxygen and the concentrations obtained in the experiments at 30°C after 72 hrs, and from equilibrium predictions. Species such as elemental sulfur, sulfides and sulfites were not measured in the analytical method;therefore complete closure of the sulfur balance was not possible, especially in acidic conditions where the reaction pathways could yield those species. Nevertheless, though sulfur was not measured directly, sulfur precipitation was observed; so even in the absence of a complete sulfur balance, the experimental observations were consistent with the HSC results where equilibrium predictions indicate that elemental sulfur is an important product of the reaction of thiosalts at acidic conditions.

In mildly acidic (pH 4) to alkaline conditions (pH 9), the sulfur mass balance is within experimental error during the experimental runs, indicating the most of the species present in solutions are measured in the analytical method.

In experiments at pH 2, at 72 hours thiosulfate is consumed, trithionate increased, and tetrathionate appears to have decreased, though based on experimental error, the decrease is not statistically relevant. This is different than HSC equilibrium predictions, which indicate that all the sulfur should be present as either sulfate or elemental sulfur, with elemental sulfur representing ~30% of the total sulfur. Experimentally, the total measured sulfur had decreased, but the discrepancy in the mass balance can be attributed to experimental error and the limit of the analysis, where some key sulfur species, particularly sulfur, are not measured. It should be noted that solid sulfur precipitate was observed and the characteristic odor of H_2S characteristic was detected.

It is assumed that the solutions are all saturated with respect to oxygen. However, in a study of thiosulfate in acidic conditions and under-saturated with respect to oxygen, it was found that thiosalt oxidation will yield sulfite (SO_3^{2-}) instead of sulfate (Xu and Schoonen (1995). During our experiments, the samples were not constantly aerated, hence it is possible that oxygen was limiting in solution and therefore; under-saturated oxygen conditions were present. This could be the reason for the low percentage of

sulfate as final product, in the solution as the oxygen required to fulfill the material balance in equilibrium is higher than its original (saturated) concentration in solution.

Table 3 Sulfur and oxygen balance in thiosalts mixtures

		Sulfur (mmol)			Oxygen (mmol)		
		@0 hrs	@ 72 hrs	Equilibrium Predictions	@0 hrs	@ 72 hrs	Equilibrium Predictions
pH 2	S_2O_3	8.9	4.7	---	13.4	7	---
	S_3O_6	7.8	8.4	---	15.6	16.8	---
	S_4O_6	8.9	7.7	---	13.4	11.5	---
	SO_4	---	0.5	17.6	---	2	70.2
	S°	---	n/a	7.7	---	---	0
	Total	25.6	21.3	25.3	42.4	37.3	70.2
pH 4	S_2O_3	8.9	10.4	---	13.4	15.6	---
	S_3O_6	7.8	6.5	---	15.6	13.1	---
	S_4O_6	8.9	7.5	---	13.4	11.2	---
	SO_4	---	0.7	17.6	---	2.8	70.2
	S°	---	n/a	7.7	---	---	0
	Total	25.6	25.1	25.3	42.4	42.7	70.2
pH 7	S_2O_3	8.9	10.5	---	13.4	15.8	---
	S_3O_6	7.8	6.4	---	15.6	12.8	---
	S_4O_6	8.9	7.2	---	13.4	10.8	---
	H_2S	---	n/a	11.7	---	3.2	0
	HS^-	---	n/a	13.5	---	---	0
	Total	25.6	24.1	25.2	42.4	42.6	0
pH 9	S_2O_3	8.9	13	---	13.4	19.5	---
	S_3O_6	7.8	7.5	---	15.6	14.9	---
	S_4O_6	8.9	6.7	---	13.4	10.1	---
	H_2S	---	n/a	18.2	---	3.1	0
	HS^-	---	n/a	7	---	---	0
	Total	25.6	27.2	25.2	42.4	47.6	0

The material balance for pH 4 for both sulfur and oxygen does close, though it is possible that other species are present in trace quantities. Thiosulfate is generated at these conditions. Single species experiments did not show reactivity and it is likely the

decreasing trithionate leads to the production of thiosulfate. The sulfate also increases marginally.

The trend and results for the sulfur and oxygen material balance at pH 7 are very similar to pH 4. This suggests that the reactions and pathways could be similar at both conditions. Also worth noting is that trithionate is the main species reacting at those conditions.

The pure species studies at pH 9 show conditions favour the generation of thiosulfate, and the consumption of tetrathionate, trithionate and oxygen. The amount of sulfur in solution increases marginally though there is no external source of sulfur in solution; this is likely due to measurement error. Despite the differences in numbers, the trends observed at pH 9 are as expected. Thiosulfate is generated as a result of the degradation of tetrathionate, on par with previous results. In the case of trithionate, its concentrationremains almost constant during the experiment despite its demonstrated reactivity under these conditions in single species experiments.This could be the result of the equality between its generation via tetrathionate decomposition and its consumption to form thiosulfate and sulfate.

With the information gathered in the material balance, the equilibrium simulations and the experimental results, global reaction pathways are proposed for thiosalts in mixtures as a function of pH, which are presented in Figure 6. Hydrogen sulfide is cautiously proposed as a terminal pathway at acidic pH, based on the fact that it wasdetected but not quantifiedduring studies of thiosulfate solutions. At neutral and alkaline conditions, hydrogen sulfide was not detected.

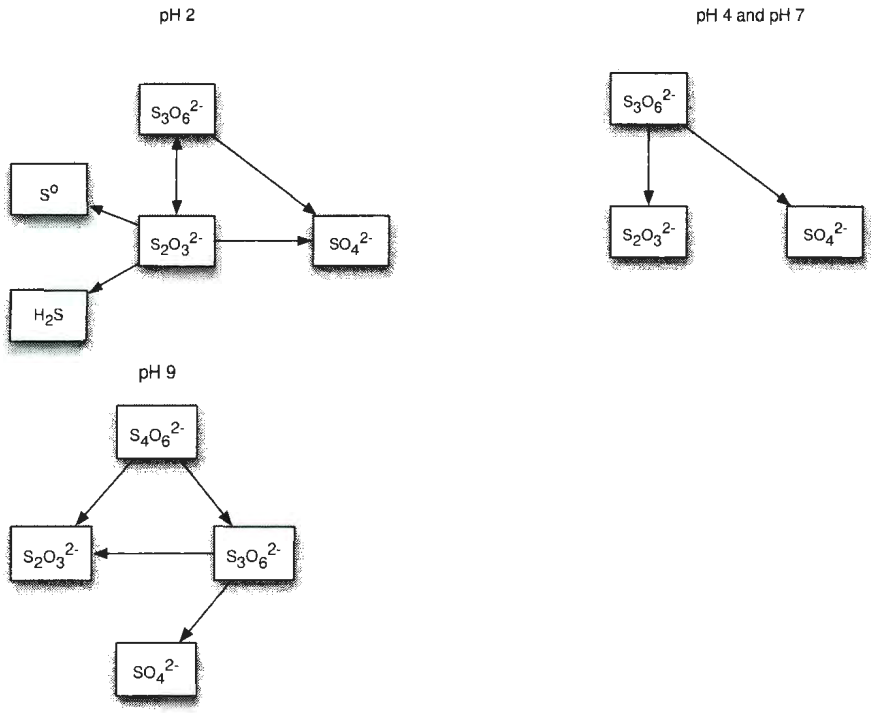


Figure 6.Global reaction pathways for thiosalts in mixtures based on experimental results.

There are a few key points that should be reiterated here. Tetrathionate is stable in the acidic and neutral (pH 2, 4 and 7)pathways. The only species reactive over the entire pH rangeis trithionate. Equilibrium simulations yield sulfur and sulfate as the final products in acidic and mildly acidic conditions, while hydrogen sulfide and bisulfide are produced in alkaline and neutral conditions. Only sulfate is an oxidized species, whereas the others (sulfur and sulfides) are the reduced sulfur forms. The proposed reaction pathways are important for reaction analysis as previous studies for pure species provide information about the decrease of pure species and the generation of products. The combination of those equations applied to the mixtures using a decoupling approachshould provide enough information to model the mixtures at different conditions.

3.4 Reaction Rate Analysis

To calculate the reaction rates for the mixture, the experimental data was optimized using the procedure explained in section 2.3; in the optimization we included the pure species term proposed by Miranda-Trevino *et al.*, 2012.

Reaction order analyses were conducted prior to the simulation using Van't Hoff's plots (Appendix A.5) to provide supporting information of the data.Overall, it can be concluded that thiosulfate will likely follow a first order, second order consumption reaction;trithionate and tetrathionate reactions will follow first order and sulfate generationwill follow a zero-order reaction. The reaction constants at all pH conditions are calculated at 30℃ as the change in concentration in the mixtures at lower temperatures were small and close to experimental error.

From the pure species analysis under acidic conditions (pH 2), thiosulfate and trithionate are reactive and produce sulfate. This is confirmed in the results of the mixture experimental data, though the degradation of thiosulfate is slower than as a pure species. With trithionate the generation and reaction rates are likely to be equal or nearly equal as the change in concentration over the time period is not statistically significant, being within the experimental error for trithionate. Using the pathway proposed in Figure 7, the kinetic analysis is as follows:

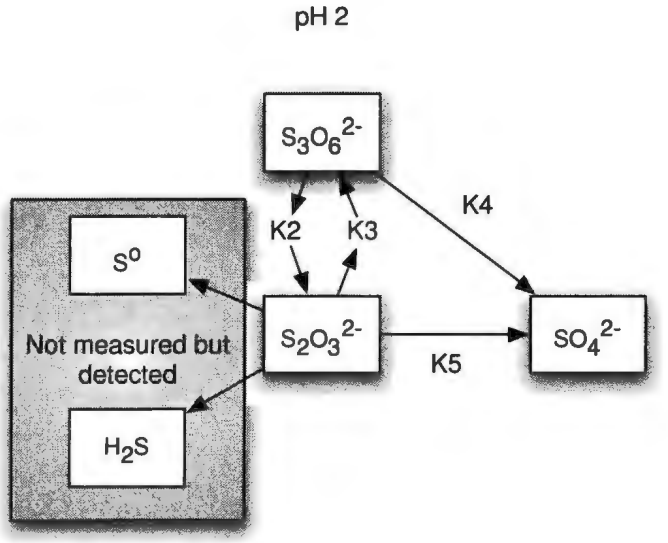


Figure 7. Thiosalts reaction pathway at pH 2

Elemental sulfur and hydrogen sulfide were formed and detected but not quantified; hence it is not possible to include them in the model. Under these conditions, thiosulfate (for net reactivity) and sulfate(for production) will be the species to model. For trithionate, it is likely that the reactions rates for consumption and production are equal, hence there is no net change in its concentration. Following the assumptions, the reaction rates for thiosalts in mixtures at pH 2 and 30℃ derived from the analysis are:

$$\frac{d[S_2O_3^{-2}]}{dt} = -2.6x10^{-2}\frac{1}{mM * h}[S_2O_3^{-2}]^2 + 5.8x10^{-2}\frac{1}{h}[S_2O_3^{-2}] \qquad (4)$$

The first terms in the reaction rate equationswere obtained from the pure species calculations. Reaction 4reflects that the thiosulfate rate of reaction in the mixture is slower when compared to pure species as it has a positive term and reaction constant; thiosulfate is likely produced from the degradation of trithionate.Comparisonsof the experimental data from the mixtures to single species and mixture simulations are presented in Figure 8.

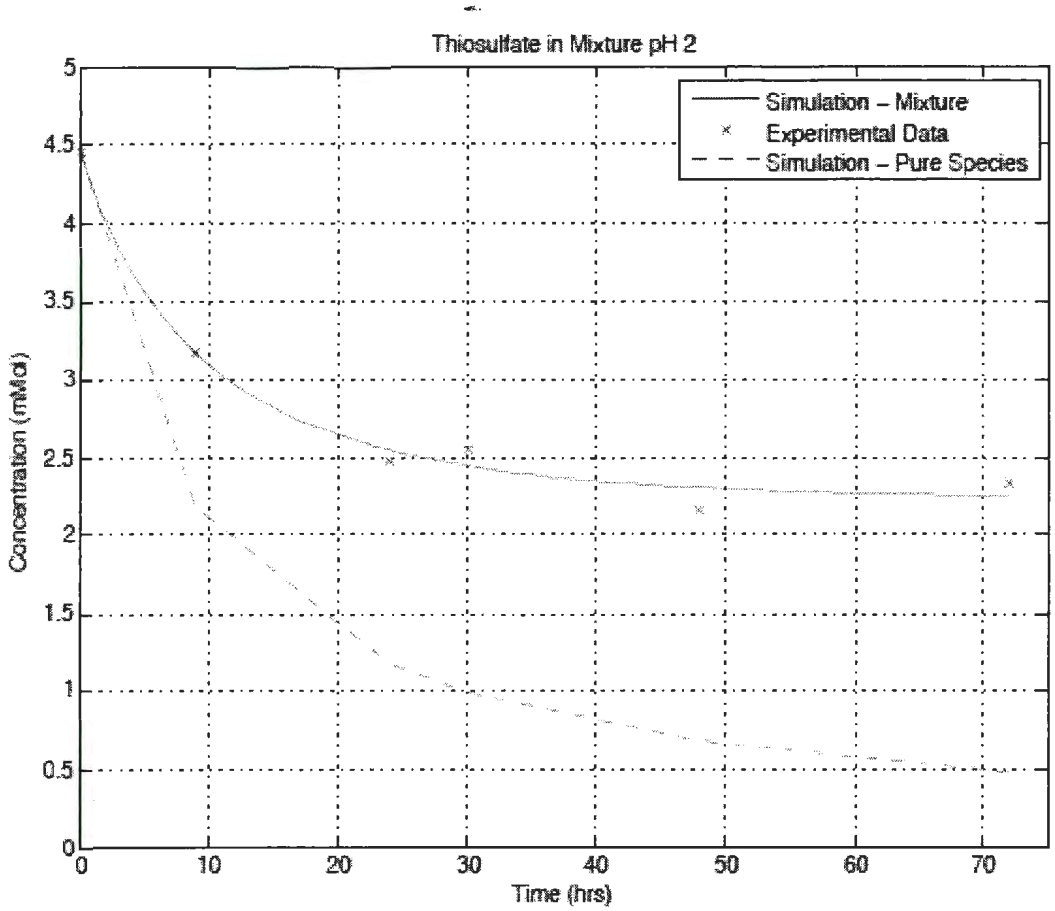


Figure 8.Plots comparing simulation and experimental results mixture at pH 2

The modeling for thiosulfate in solution yieldedresults in agreement with the concentrations measured in the experiments.The soundness of the fit between the model and the experiments is illustrated particularly well for thiosulfate, where the concentration change is much slower when in a mixture of thiosalts.A more extensive analysis of the reaction mechanisms in solution is required to understand the reason why the reaction rate for thiosulfate in mixture is around 80% slower than as a pure species.

The behavior of the mixtures at pH 4 and 7 is fairly consistent, and the reaction rates obtained for all of the sulfur species are very close. A key characteristic of these

conditions is that the only reactive species is trithionate, so the kinetic analysis is simplified as shown in Figure 9.

pH 4 and pH 7

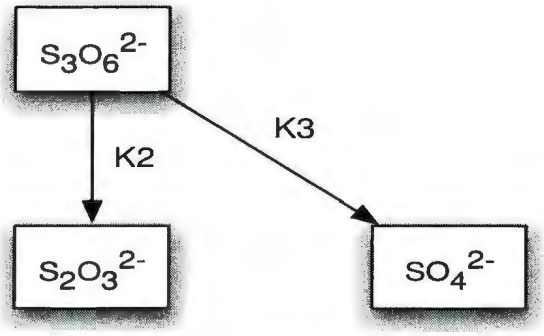


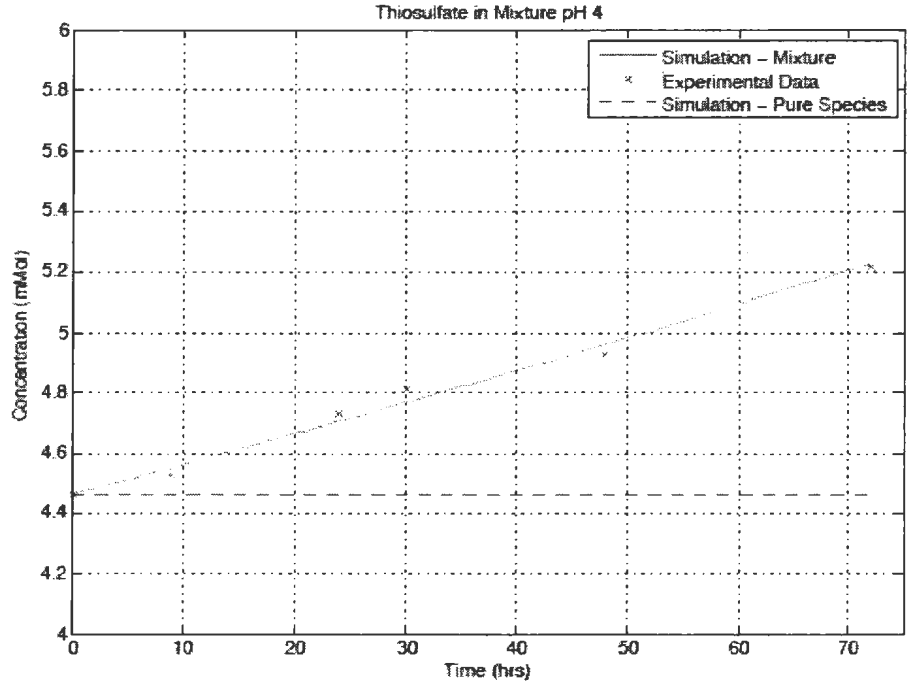
Figure 9. Thiosalts reaction pathway at pH 4 and 7

Similar to thiosulfate at pH2, trithionate degradation is slower in mixture than as pure species; this is mainly attributable to generation of trithionate as tetrathionate is consumed. Equations5 and 6 represent the behavior of the sulfur species in mixtures at pH 4; comparisonsof pure species and mixtures simulations with experimental data are shown in Figure 10.

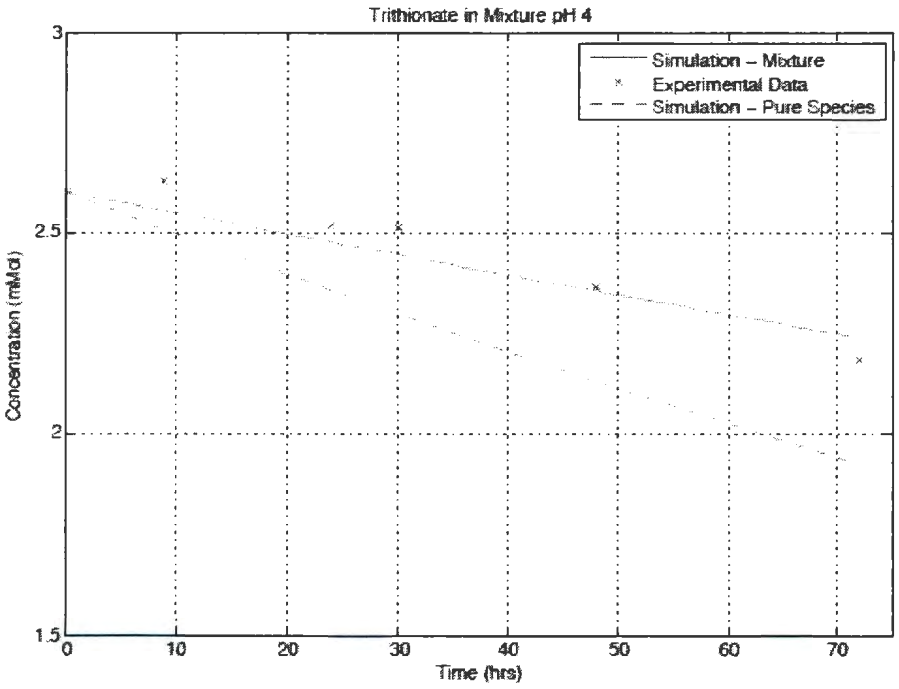
$$\frac{d[S_2O_3^{-2}]}{dt} = 2.2x10^{-3}\frac{1}{h}[S_2O_3^{-2}] \quad (5)$$

$$\frac{d[S_3O_6^{-2}]}{dt} = -4.2x10^{-3}\frac{1}{h}[S_3O_6^{-2}] + 2.1x10^{-3}\frac{1}{h}[S_3O_6^{-2}] \quad (6)$$

As expected, trithionate is the main reactive species,and thiosulfate isproduced in the solution.



(a)



(b)

Figure 10. Plots comparing simulation and experimental results mixture at pH 4

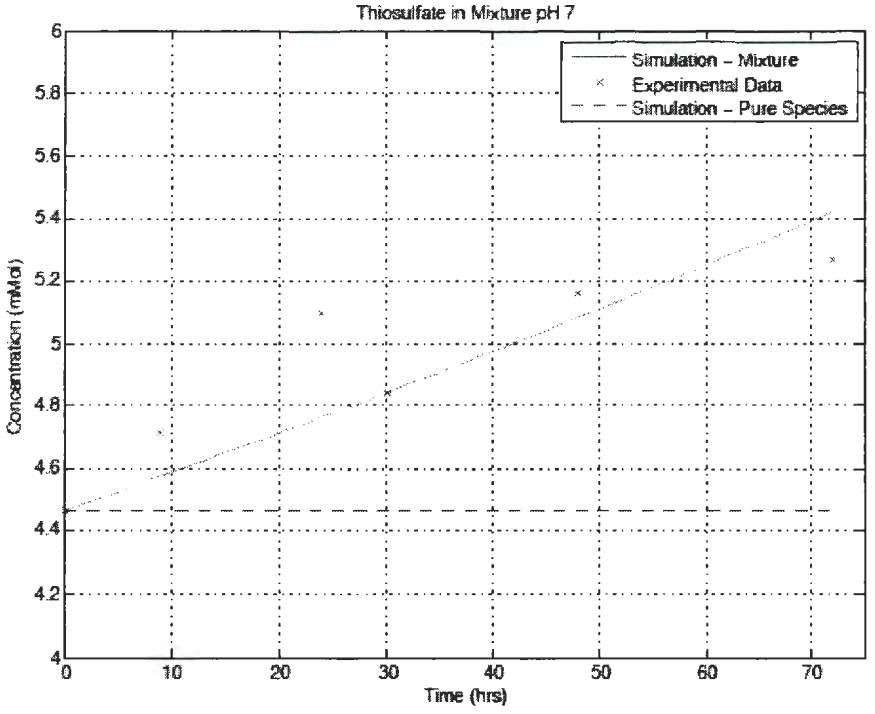
The plots show good agreement between the experimental and predicted values. One reason for the goodness of the fit is the lack of dispersion on the experimental data. Also, there are no "cycles" (i.e. thiosulfate reacting to trithionate and vice-versa) present at these conditions, hence the complications are minimal.

The equations proposed for pH 7 are very similar to pH 4 as shown in equations 7 and 8.

$$\frac{d[S_2O_3^{-2}]}{dt} = 2.7x10^{-3}\frac{1}{h}[S_2O_3^{-2}] \tag{7}$$

$$\frac{d[S_3O_6^{-2}]}{dt} = -4.1x10^{-3}\frac{1}{h}[S_3O_6^{-2}] + 1.9x10^{-3}\frac{1}{h}[S_3O_6^{-2}] \tag{8}$$

The plots comparing experimental and predicted data are shown in Figure 11.



(a)

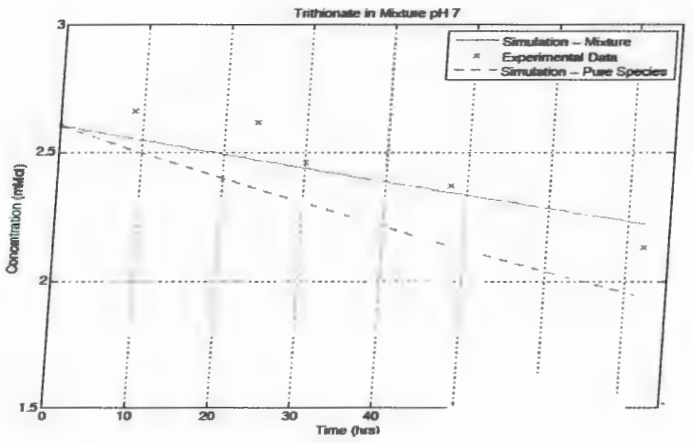


Figure 11. Plots comparing simu- 7

The reaction ra- th the
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e- ate
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conditions is that the only reactive species is trithionate, so the kinetic analysis is simplified as shown in Figure 9.

pH 4 and pH 7

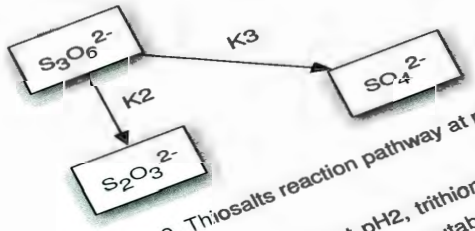

Figure 9. Thiosalts reaction pathway at pH 4 and 7

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$$\frac{d[S_3O_6^{-2}]}{dt} = -4.2x10^{-3}\frac{1}{h}[S_3O_6^{-2}] + 2.1x10^{-3}\frac{1}{h}[S_3O_6^{-2}] \quad (6)$$

As expected, trithionate is the main reactive species,and thiosulfate isproduced in the solution.

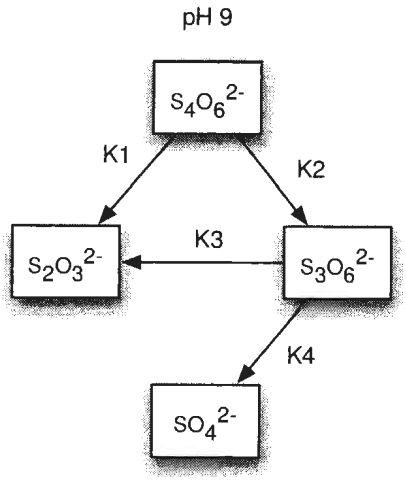
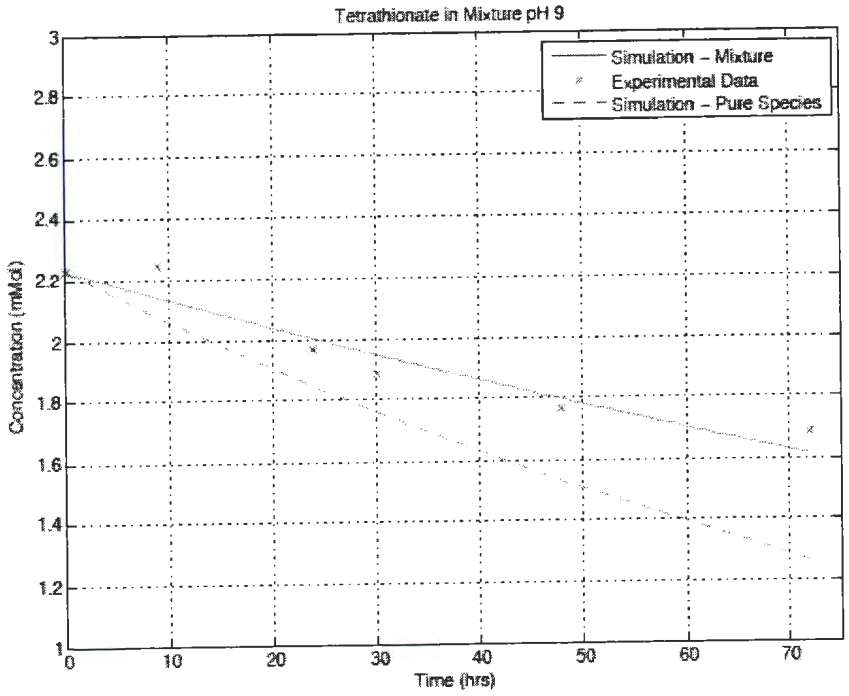


Figure 12. Thiosalts reaction pathways at pH 9

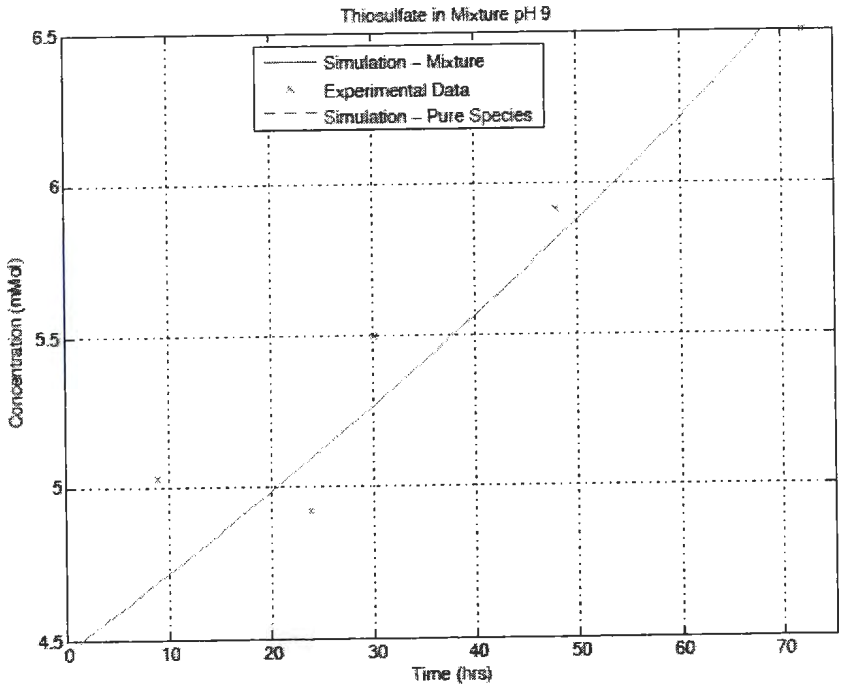
Equations 9 and 10 show the reaction rates of the different sulfur species at pH 9, while Figure 13 compares the simulated and experimental data comparison (pure species results are zero as thiosulfate was not reactive at pH 9).

$$\frac{d[S_2O_3^{-2}]}{dt} = 5.5x10^{-3}\frac{1}{h}[S_2O_3^{-2}] \quad (9)$$

$$\frac{d[S_4O_6^{-2}]}{dt} = -7.9x10^{-3}\frac{1}{mM*h}[S_4O_6^{-2}] + 3.4x10^{-3}\frac{1}{mM*h}[S_4O_6^{-2}] \quad (10)$$



(a)



(b)

Figure 13. Plots comparing simulation and experimental results mixture at pH 9

The generation of thiosulfatein alkaline conditions is higher than thatfor neutral and mildly acidic conditions. This means that thiosulfate generation through the tetrathionate pathway is higher than via trithionate; nevertheless the model underestimates thiosulfate concentration. The material balances do show an excess in total sulfur in the solution at 72 hrs (compared to the starting mass balance), so it is likely that there is an error in the estimation of thiosulfate in the lab data, giving higher concentrations than are present in solution. In the case of trithionate, the change in concentration is within the analytical error, which indicates that there is limited activity at these conditions or that there is equilibrium between the generation and degradation reaction rates.

Tetrathionate predicted values show good agreement with the experimental values. As in the previous examples, the reaction rate is slower than as a pure species. A more in-depth study outside the scope of this paper is required to understand the reasons of the difference in rates in species and species.

Despite the challenges faced in the study of thiosalt mixtures, it is possible to provide a mathematical model that can be used to predict the behavior of the three major sulfur species at 30°C and in a pH range of 2 to 9.

4. Conclusions

The development of the reaction rate equations for thiosalt mixture at different pH conditions was possible for the thiosalt species. The equations proposed show good agreement with the data gathered in the lab and provide useful information regarding the potential global reaction pathways in mixtures. Similar to studies done with pure sulfur species, the equilibrium products for thiosalt reaction mixtures under temperature conditions of the pond are elemental sulfur and sulfate in acidic/mildly acidic conditions and sulfides (hydrogen sulfide and bisulfide) under neutral and alkaline conditions. For all cases, the reaction rates were slower in mixtures than as pure species; this could be the result of cyclic reaction pathways.

The modeling of mixtures is challenging, however, by applying the decoupling approach with the selection of reference species at the different pH conditions, it was possible to propose reaction rates that agreed with data collected in the lab for all the main species.

Using equilibrium analyses and the material mass balances, it was possible to provide global reaction pathways for thiosalts in a mixture. The pathways can be classified into three groups: acidic (pH 2), mildly acidic and neutral (pH 4 and 7) and alkaline (pH 9). At acidic conditions, the key sulfur species is thiosulfatewith a contribution from trithionate. At pH 4 and 7, trithionate is the dominant species reacting, while at alkaline condition tetrathionate is most reactive.The presence of hydrogen sulfide was noted by odor in experiments and therefore additional analysis is required to determine thereaction mechanism. This is important, as hydrogen sulfide is toxic and would provide valuable insight into the overall pathway.

In terms of the material mass balance, conditions that show sulfur precipitates from the solution during the experimental runs were at pH 2. The presence of elemental sulfur and hydrogen sulfide was qualitatively observed. However, some of the difference in sulfur concentration at low pH could be due to the presence of sulfite, which was not quantified, or due to the presence of other sulfur species not measured in the lab.The difference in the oxygen concentration required to achieve the complete oxidation of the sulfur mixture is another issue that requires further analysis to determine the origin of that oxygen and the potential routes in case of under-saturated conditions.

As noted in the reactions rates, the reactivity of each thiosalt species will depend on the pH of the solution, with thiosulfate reacting at acidic pH, tetrathionate in alkaline conditions and trithionate reacting in the whole pH range. It is also important to note that thiosalt behavior is different in a solution with thiosalt mixtures than as a pure species, usually yielding slower reaction rates in mixtures. The reaction models proposed for the thiosalt mixtures provide a starting point in the environmental risk assessment and the evaluation of treatment technologies.

5. References

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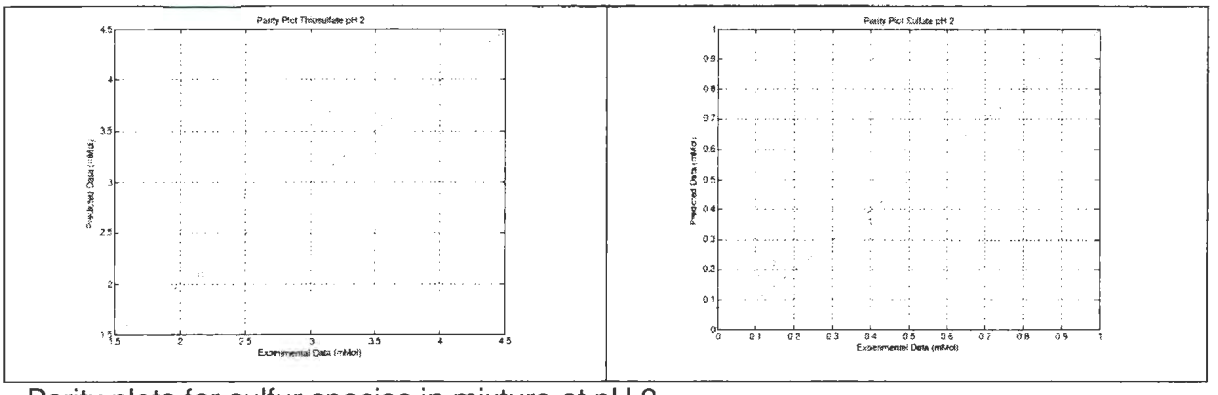
Appendices

A.1Pure Species Reaction Rates

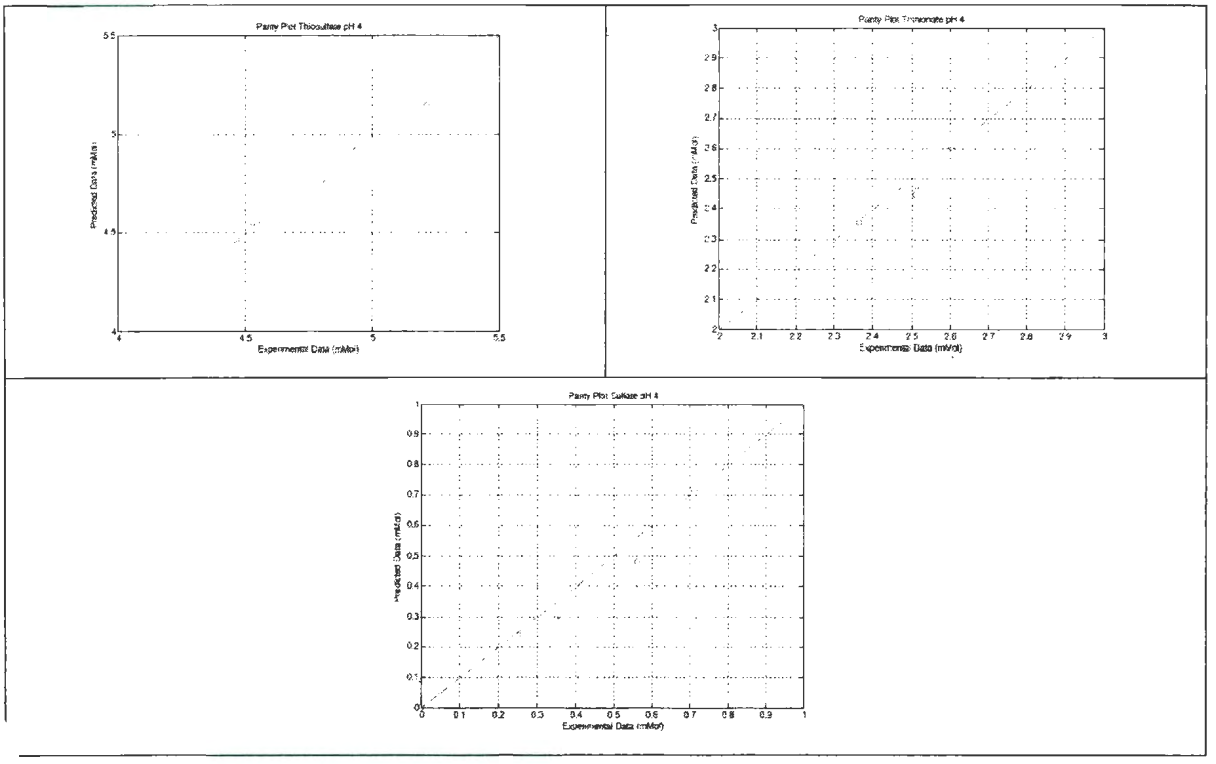
pH	Initial Sulfur Species	Reaction Rates
2	$S_2O_3^{2-}$	$-\frac{d[S_2O_3^{-2}]}{dt} = 2.6x10^{-2}\frac{1}{mM*h}[S_2O_3^{-2}]^2$ $\frac{d[S_3O_6^{-2}]}{dt} = 1.2x10^{-2}\frac{mM}{h}$ $\frac{d[SO_4^{-2}]}{dt} = 1.0x10^{-2}\frac{mM}{h}$
	$S_3O_6^{2-}$	$\frac{d[S_2O_3^{-2}]}{dt} = 5.7\text{x}10^{-3}\frac{mM}{h}$ $-\frac{d[S_3O_6^{-2}]}{dt} = 3.2x10^{-3}\frac{1}{h}[S_3O_6^{-2}]$ $\frac{d[SO_4^{-2}]}{dt} = 9.5\text{x}10^{-3}\frac{mM}{h}$
4	$S_3O_6^{2-}$	$\frac{d[S_2O_3^{-2}]}{dt} = 1.9\text{x}10^{-2}\frac{mM}{h}$ $-\frac{d[S_3O_6^{-2}]}{dt} = 4.2x10^{-3}\frac{1}{h}[S_3O_6^{-2}]$ $\frac{d[SO_4^{-2}]}{dt} = 2.0\text{x}10^{-2}\frac{mM}{h}$
7	$S_3O_6^{2-}$	$\frac{d[S_2O_3^{-2}]}{dt} = 1.9\text{x}10^{-2}\frac{mM}{h}$ $-\frac{d[S_3O_6^{-2}]}{dt} = 4.1x10^{-3}\frac{1}{h}[S_3O_6^{-2}]$ $\frac{d[SO_4^{-2}]}{dt} = 2.1\text{x}10^{-2}\frac{mM}{h}$
9	$S_4O_6^{2-}$	$\frac{d[S_2O_3^{-2}]}{dt} = 2.7\text{x}10^{-2}\frac{mM}{h}$ $\frac{d[S_3O_6^{-2}]}{dt} = 1.1x10^{-2}\frac{mM}{h}$ $-\frac{d[S_4O_6^{-2}]}{dt} = 7.9x10^{-3}\frac{1}{h}[S_4O_6^{-2}]$ $\frac{d[SO_4^{-2}]}{dt} = 1.9\text{x}10^{-3}\frac{mM}{h}$

	$S_3O_6^{2-}$	$\frac{d[S_2O_3^{-2}]}{dt} = 1.1x10^{-2}\frac{mM}{h}$ $-\frac{d[S_3O_6^{-2}]}{dt} = -1.9x10^{-3}\frac{1}{mM*h}[S_3O_6^{-2}]$ $\frac{d[SO_4^{-2}]}{dt} = 2.4x10^{-2}\frac{mM}{h}$

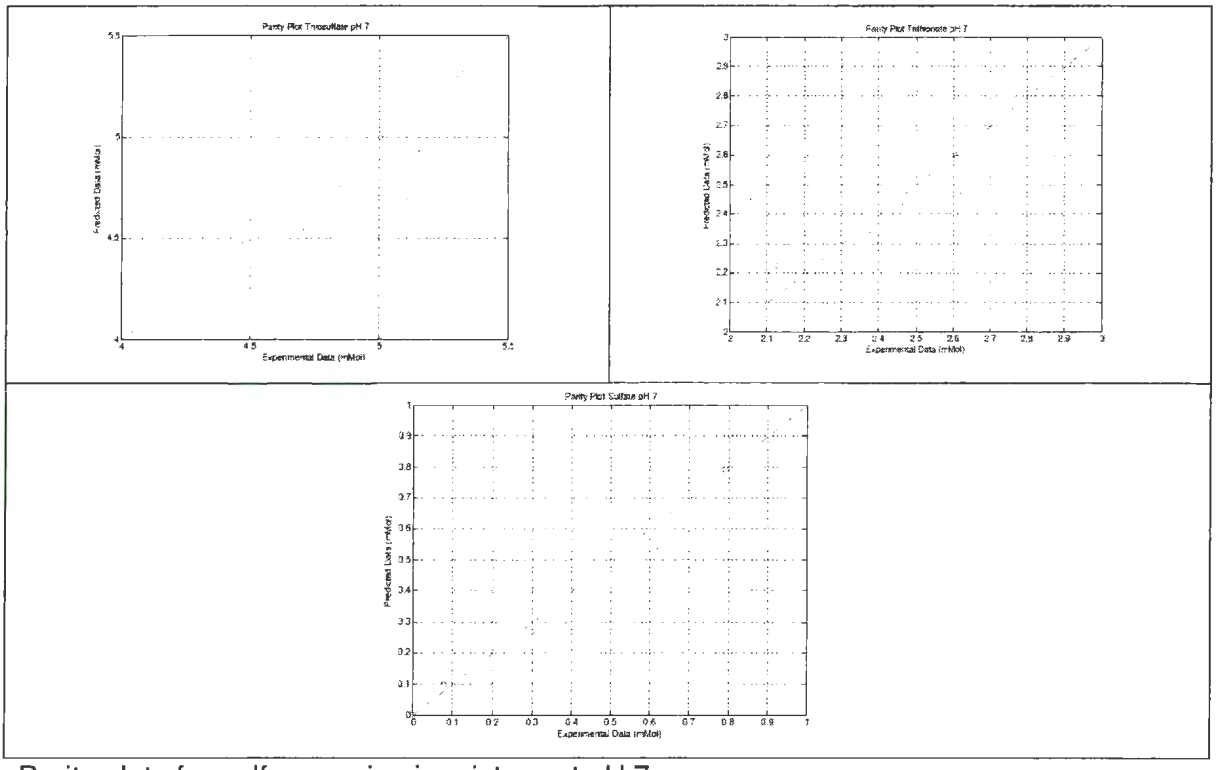
A.2 Parity Plots



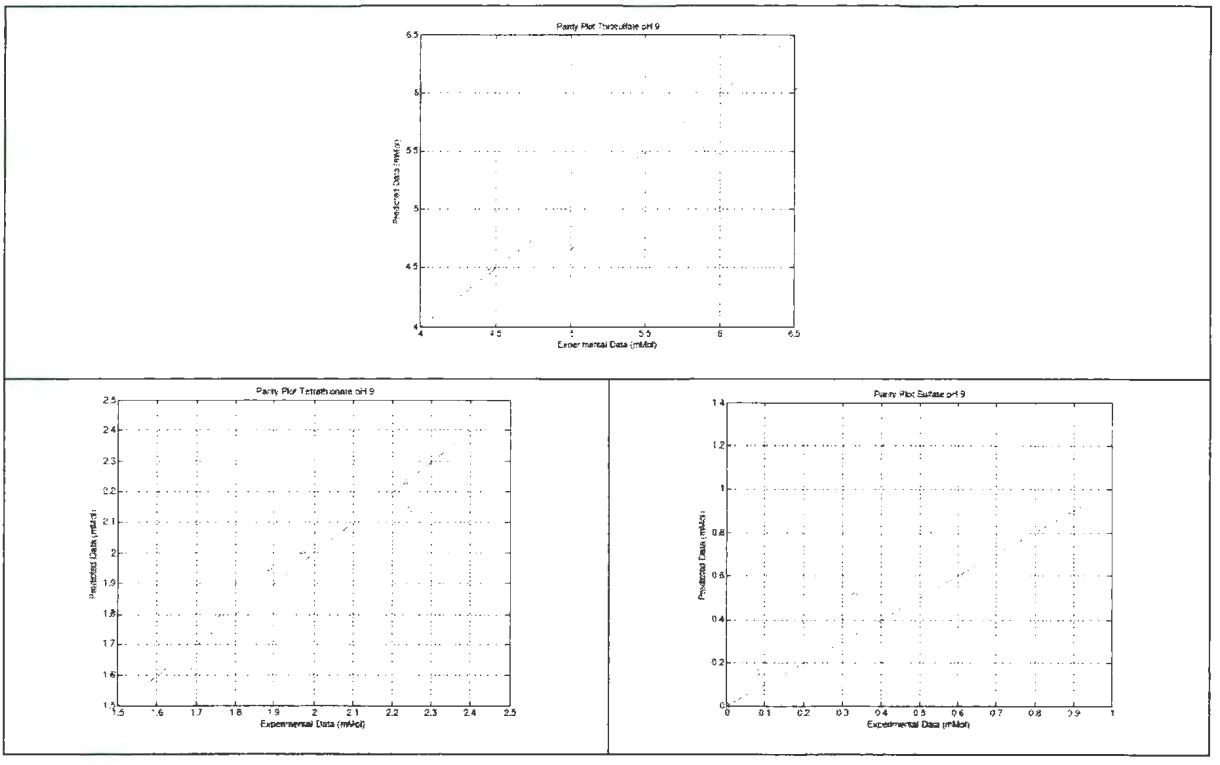
Parity plots for sulfur species in mixture at pH 2



Parity plots for sulfur species in mixture at pH 4



Parity plots for sulfur species in mixture at pH 7



Parity plots for sulfur species in mixture at pH 9

A.3 Data from pure species experiments

Thiosalt	Initial Concentration	Rxn Time	pH	Temperature (°C)	Thiosulphate (ppm)	Trithionate (ppm)	Tetrathionate (ppm)	Sulphate (ppm)
Trithionate	1000	0	2	30	0	1000	0	10
Trithionate	1000	6	2	30	8	930	2	16
Trithionate	1000	24	2	30	22	917	5	35
Trithionate	1000	48	2	30	35	864	10	57
Trithionate	1000	72	2	30	40	806	10	72
Trithionate	1000	0	4	30	0	1000	0	0
Trithionate	1000	6	4	30	13	977	0	18
Trithionate	1000	24	4	30	58	903	2	53
Trithionate	1000	48	4	30	101	806	4	99
Trithionate	1000	72	4	30	149	752	7	135
Trithionate	1000	0	7	30	3	1000	0	0
Trithionate	1000	6	7	30	19	965	1	9
Trithionate	1000	24	7	30	59	898	3	53
Trithionate	1000	30	7	30	74	886	3	
Trithionate	1000	48	7	30	112	825	7	101
Trithionate	1000	72	7	30	147	743	16	142
Trithionate	1000	0	9	30	14	1000	5	0
Trithionate	1000	7	9	30	17	984	1	23
Trithionate	1000	24	9	30	45	962	3	58
Trithionate	1000	48	9	30	76	926	3	108
Trithionate	1000	72	8	30	103	858	8	168

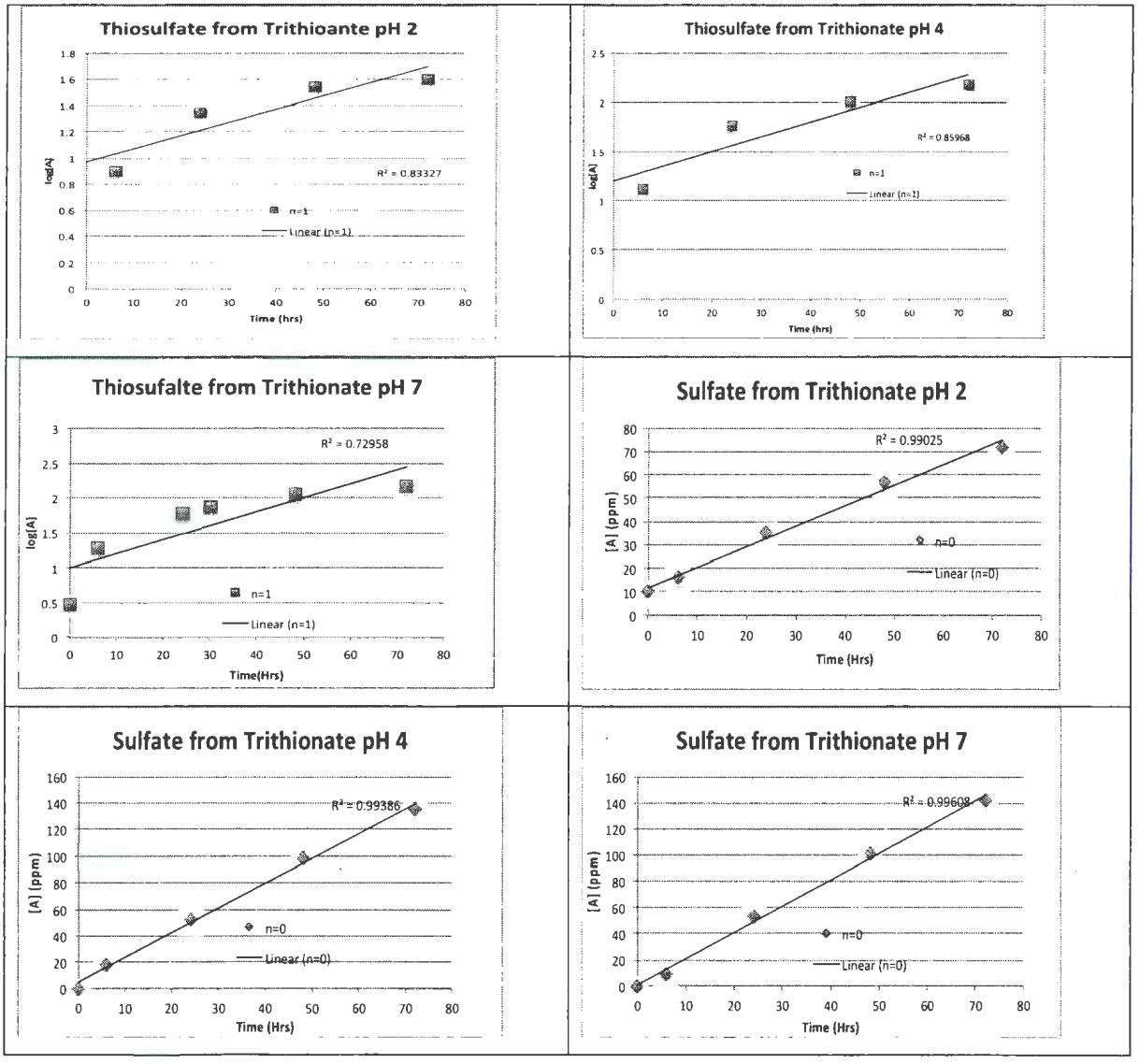
Thiosalt	Initial Concentration	Rxn Time	pH	Temperature (°C)	Thiosulphate (ppm)	Trithionate (ppm)	Tetrathionate (ppm)	Sulphate (ppm)
Tetrathionate	1000	0	9	30	6	6	1000	0
Tetrathionate	1000	6	9	30	59	25	909	0
Tetrathionate	1000	24	9	30	99	76	788	0
Tetrathionate	1000	30	9	30	117	88	764	0
Tetrathionate	1000	48	9	30	166	131	707	8
Tetrathionate	1000	72	9	30	229	178	599	14
Tetrathionate	1000	96	9	30	262	188	463	21

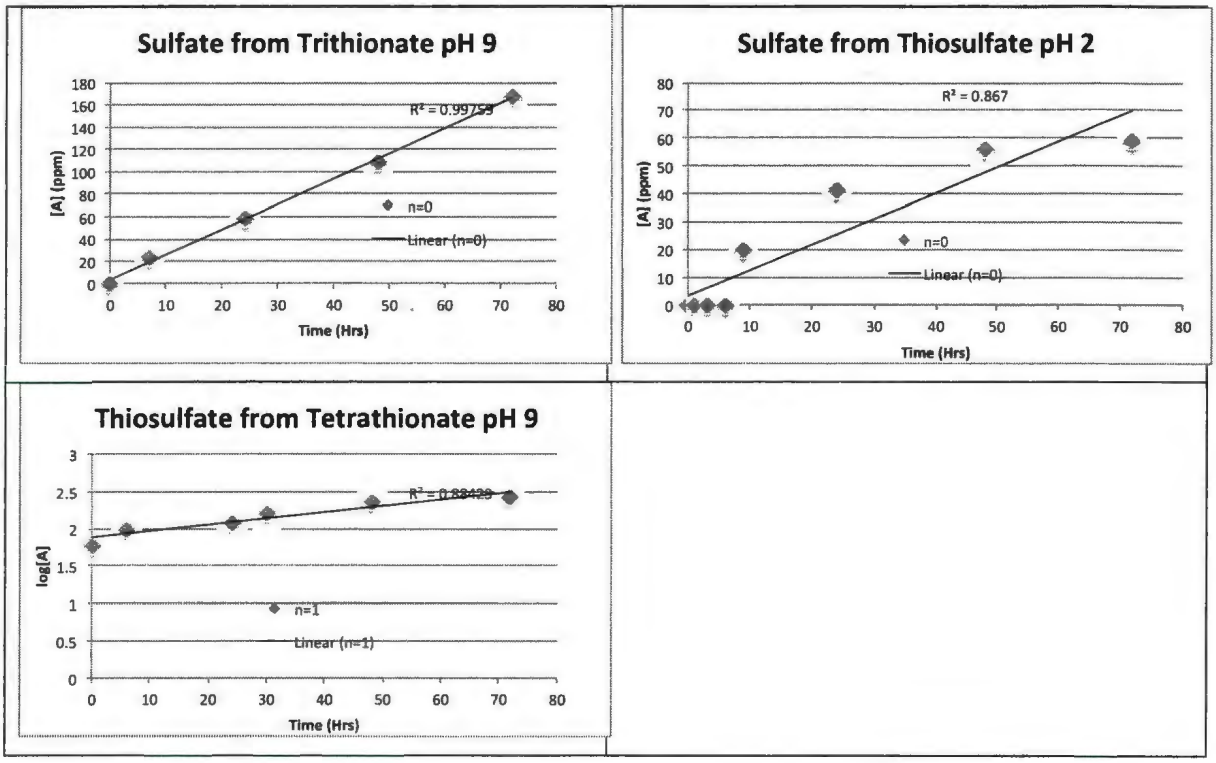
Thiosalt	Initial Concentration	Rxn Time	pH	Temperature (°C)	Thiosulphate (ppm)	Trithionate (ppm)	Tetrathionate (ppm)	Sulphate (ppm)
Thiosulphate	1000	0	2	30	1000	1	5	0
Thiosulphate	1000	1	2	30	752	7	2	0
Thiosulphate	1000	3	2	30	507	28	1	0
Thiosulphate	1000	6	2	30	385	45	1	0
Thiosulphate	1000	9	2	30	330	56	1	20
Thiosulphate	1000	24	2	30	262	96	2	41
Thiosulphate	1000	48	2	30	244	125	13	56
Thiosulphate	1000	72	2	30	220	131	23	59

A.4 Mixture Data from Experiments

pH 2 Temp 30 C				
time (hrs)	Thio (ppm)	Tri (ppm)	Tetra (ppm)	Sulfate (ppm)
0	500	500	500	0
9	355	577	431	0
24	277	574	436	11
30	285	572	397	14
48	242	523	452	38
72	261	537	429	47
pH 4 Temp 30 C				
time (hrs)	Thio (ppm)	Tri (ppm)	Tetra (ppm)	Sulfate (ppm)
0	500	500	500	0
6	507	505	470	0
24	530	483	450	24
30	539	482	437	
48	552	454	430	54
72	584	419	419	68
pH 7 Temp 30 C				
time (hrs)	Thio (ppm)	Tri (ppm)	Tetra (ppm)	Sulfate (ppm)
0	500	500	500	0
6	528	511	479	
24	571	502	445	30
30	542	472	430	
48	578	455	423	60
72	590	409	402	76
pH 9 Temp 30 C				
time (hrs)	Thio (ppm)	Tri (ppm)	Tetra (ppm)	Sulfate (ppm)
0	500	500	500	0
7	563	483	503	
24	551	485	441	29
30	616	497	423	
48	662	510	395	51
72	728	477	377	74

A.5 Van't Hoff Plots




Sulfate from Trithionate pH 9
[A] (ppm)
Time (Hrs)
R² = 0.99759
n=0
Linear (n=0)
Sulfate from Thiosulfate pH 2
[A] (ppm)
Time (Hrs)
R² = 0.867
n=0
Linear (n=0)
Thiosulfate from Tetrathionate pH 9
log[A]
Time (Hrs)
n=1
Linear (n=1)

Chapter 4

Thiosaltsreactionswith copper complexes, pyrite, ferric sulfate and hydroxyl ions.

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Abstract

The generation of acid mine drainage from thiosalt oxidation is a concern in the mining industry. In previous studies, reaction rate equationswere developed for different pH and temperature conditions and relatively simple mixtures to model the oxidation of the main thiosalt species, namely thiosulfate, trithionate and tetrathionate. However, mining waters are chemically complex, and the presence of treatment chemicals and other compounds can also impact thiosalt reactivity. Current industry practices rely on the use of either strong oxidant agents, such as hydrogen peroxide with a ferric catalyst, or natural degradation for thiosalt treatment, however, the efficacy of these treatment methods are typically based on simple mass balances, total thiosalts, and assumptions with respect to reaction rates. There has been little study of the actual reaction rates and the impact of treatment reagents on individual thiosalt species. The current paper presents a brief summary of thiosalt reactions with ferric sulfate, copper complexes and hydrogen peroxide and the results of preliminary experiments studying the reactions of thiosulfate and trithionate with hydrogen peroxide. Equilibrium calculations for thiosulfate, trithionate, tetrathionate and the mixture of the three thiosalts at temperatures ranging between 4 and 30℃ and pH between 2 and 9 are presented. Finally, a path forward in the study of thiosalts with treatment reagents is discussed.

1. Introduction

Thiosalts are partially oxidized sulfur minerals generated in the mining and processing of ores, (Wasserlauf and Dutrizac, 1982; Schippers et al., 1996; Sasaki et al,, 1995; Paschka and Dzombak, 2004; Johnson, 2003). The stable species under typical tailing pond conditions are thiosulfate ($S_2O_3^{2-}$), trithionate ($S_3O_6^{2-}$) and tetrathionate ($S_4O_6^{2-}$) (Wasserlauf and Dutrizac, 1982). Thiosalts are generated in the processing of sulfide ores, especially those involving pyrite and pyrrhotite ores, which are the most common sulfide minerals in mining operations (Moses et al., 1987). The oxidation of residual sulfide ores in the mine residue and ore in dumps has been identified as one of the key precursors of acid mine drainage (AMD), which can lead to environmental problems such as acidification of receiving waters and metal leaching (Druschel et al., 2004; Johnson, 2003; Tiwary, 2001). During the sulfide oxidation process, thiosalts play an important role in the generation of protons that decrease the pH of the watersheds. Studies from Schwartz et al. (2006) and Yaschyhyn (2006) regarding thiosalt toxicity support the industry consensus that the main environmental concern from these species is pH depression. Concentrations of thiosalts in typical effluent from sulfide mineral mines can result in a pH depression as low as 2 (Rolia and Tan, 1985), high sulfate concentrations and high metal loading, especially iron (Tiwary, 2001).

The use of catalysts or reagents for thiosalt oxidation in the pond is extremely important to accelerate their reaction rates. Pyrite participate in thiosulfate formation but also enhances thiosulfate oxidation by promoting the interaction of the thiosalt with oxygen on its surface, yielding tetrathionate as the main product (Borda et al., 2004; Brimblecome, 2005; Druschel et al., 2004; Garcia et al.., 2005; Johnson, 2003; Xu and Schoonen, 1995, Rimstidt and Vaughan, 2003):

$$FeS_2 + H^+ + 3H_2O \rightarrow S_2O_3^{2-} + Fe^{2+} + 7H^+ \quad (1)$$

$$S_2O_3^{2-} + 0.5O_2 + 2H^+ \rightarrow S_4O_6^{2-} + 2H_2O \quad (2)$$

Reaction 1 shows that pyrite degradation produce thiosulfate, however, at acidic pH, thiosulfate will undergo further oxidation to tetrathionate with pyrite acting as catalyst to the reaction. (Druschell et al. 2003b; Xu and Schoonen, 1995). The formation rate of tetrathionate in the presence of pyrite between pH of 2.2 and 6.9 has been described in the following way (Xu and Schoonen, 1995):

$$R_{S_4O_6^{-2}} = K[FeS_2][S_2O_3^{-2}]^n \quad (1)$$

Where the reaction order is between 0 and 1, depending on the thiosulfate/pyrite ratio, and the reaction constant is on average $6x10^{-8}$ $Mm^{-2}sec^{-1}$. In the absence of catalysts, tetrathionate will be stable in acidic and neutral solutions (Xu and Schoonen, 1995) or with very limited reactivity in mixtures (Miranda-Trevino et al., 2012a).

Like pyrite, Fe^{3+} will also act as a catalyst for thiosulfate reaction yielding tetrathionate as a product in acidic environments according to the following reaction (Druschell et al., 2003a):

$$2S_2O_3^{2-} + 2Fe^{3+} \rightarrow 2FeS_2O_3^{+} \rightarrow S_4O_6^{2-} + 2Fe^{2+} \quad (3)$$

Under certain conditions, trithionate can also be catalyzed by Fe^{3+} in the presence of oxygen according to the following reaction (Druschell et al., 2003a):

$$S_3O_6^{2-} + Fe^{3+} + \tfrac{1}{2}O_2 \rightarrow S_2O_3^{2-} + SO_4^{2-} + Fe^{2+} \quad (4)$$

Druschell et al. (2003a) reported an initial reaction rate of $2x10^{-7}$ mol $L^{-1}s^{-1}$ at a temperature of 35°C and pH of 1.5. A similar reaction is proposed for tetrathionate, however, Druschell et al. (2003a) also concluded that oxygen is a better oxidant than Fe^{3+} for tetrathionate:

$$4S_4O_6^{2-} + 3Fe^{3+} + 2.75O_2 + 4.5H_2O \rightarrow 4SO_4^{2-} + 3Fe^{2+} + 9H^{+} \quad (5)$$

Another metal that has been studied for its catalytic effect on thiosalts is copper. The thiosulfate reaction pathway in the presence of oxygen and copper as proposed by Chanda and Rempel (1987) is shown in Figure 1.

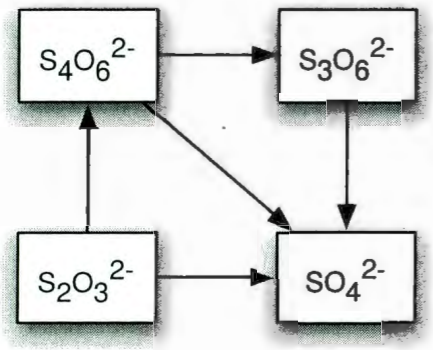

Figure 1. Reaction pathways of thiosulfate to sulfate in the presence of copper complexes (Chanda and Rempel, 1987).

At moderately high temperatures (between 40 and 60℃) and acidic conditions, thiosulfate and tetrathionate will oxidize to sulfate in the presence of copper and oxygen. The reaction is reported to be pseudo first-order, where k_1 and k_2 depend on the temperature and CuS or Cu_2S presence according to Table 1 (Chanda and Rempel, 1987):

$$\frac{d[S_2O_3^{-2}]}{dt} = -(K_1 + K_2)[S_2O_3^{-2}] \quad (2)$$

Table 1. Rate constants for thiosulfate degradation in the presence of copper (modified from Chanda and Rempel, 1987)

Temp (°C)	Catalyst			
	CuS		Cu_2S	
	Rate Constant, k x 10^2 min^{-1}			
	k_1	k_2	k_1	k_2
40	2.36	0.4	2.99	0.95
50	5.1	0.86	5.01	1.8
60	11.34	2.04	9.1	3.7

Chanda and Rempel (1987) also suggested that the oxidation of tetrathionate at alkaline conditions would go through trithionate to sulfate; however, it is unclear if copper species have a catalytic effect on the reaction rate.

A common chemical used in the thiosalt treatment is hydrogen peroxide (Dinardo and Sally, 1998). Previous studies show that trithionate reactivity with hydrogen peroxide is limited but it can be improved with the addition of iron(III) to generate the Fenton reagent (Druschell et al., 2003b). This technology has been adopted in recent years as the preferred method to treat thiosalts, despite the cost involved in the use of H_2O_2 (Kuyucak, 2006). Similarly, hydrogen peroxide does not effectively enhance the oxidation rate of tetrathionate either (Druschell et al. 2003b) but hydroxyl radicals, do promote the oxidation, outlined by the following half reactions:

$$S_4O_6^{2-} + 10H_2O \rightarrow 4SO_4^{2-} + 14e^- + 2OH^+ \quad (6)$$

$$OH^{\bullet} + 1e^- + H^+ \rightarrow H_2O \quad (7)$$

Druschell et al. (2003b) proposed an intermediate for the reaction of the form $HS_3O_4^{n-}$. This oxidation reaction can be considered to be second-order rate constant and a reaction constant of the order of 10^8. The reaction pathway proposed is shown in Figure 2.

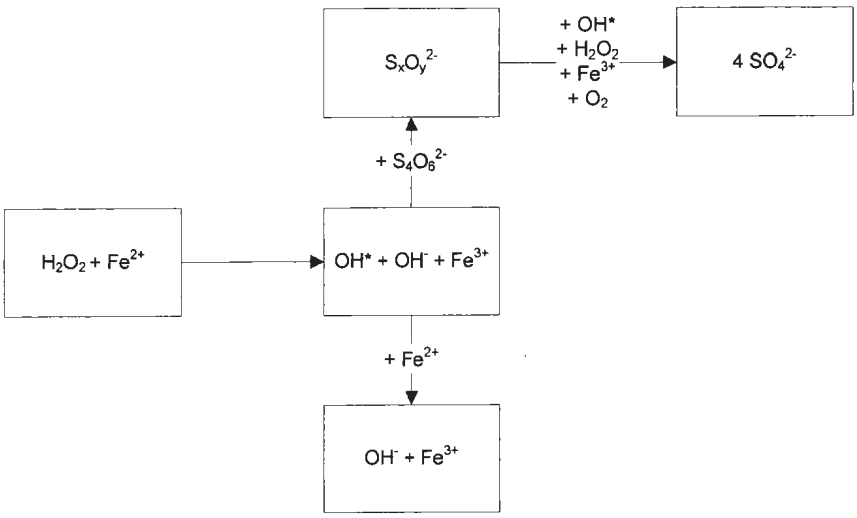

Figure 2..Reaction pathway for tetrathionate in the presence of Fe^{3+} at low pH (Modified from Druschell, 2003b)

In the case of alkaline environments, Voslar et al. (2006) identified thiosulfate as a key intermediate in tetrathionate oxidation by hydrogen peroxide according to the following reactions:

$$S_4O_6^{2-} + 2H_2O_2 + 4OH^- \rightarrow S_2O_3^{2-} + 4SO_4^{2-} + SO_3^{2-} + 4H_2O \quad (8)$$

$$S_4O_6^{2-} + SO_3^{2-} \rightarrow S_2O_3^{2-} + S_3O_6^{2-} \quad (9)$$

And a reaction rate of:

$$\frac{d[S_4O_6^{-2}]}{dt} = -1.5x10^{-2}(M^2s)^{-1}[S_4O_6^{-2}][H_2O_2][OH^-] \quad (3)$$

The behavior and reaction kinetics for thiosalts in solutions without the presence of catalyst have been studied before (Miranda-Trevino et al 2012b). However, it is important to identify the effects that reagents present in the pond could present in the reaction rates under the typical temperature and pH ranges of tailing ponds in order to develop better water treatment and management options for mining sites. This paper

presents an equilibrium analysis for thiosalts in the presence of selected reagents, as well as a comparison of preliminary data for some reagents with published data. The objective is to provide background information for further thiosalt studies (either as pure species or mixtures) in the presence of reagents such as pyrite, iron, copper or hydrogen peroxide.

2. Materials and Methods

2. 1 Batch Studies

Thiosalts were mixed in solution following the procedure developed by Miranda-Trevino et al. (2012b). Three thiosalts were studied: thiosulfate, trithionate and tetrathionate. Sodium thiosulphate pentahydrate from Merck and potassium tetrathionate from Sigma-Aldrich were used during the experiments. Trithionate is not commercially available and was synthesized using a modified Kelly and Wood (1994) method. The pH of the solutions was maintained using buffer solutions. For pH 2 dilute acetic acid: glacial acetic acid diluted until the pH reached 2; the pH 4 buffer used 50 mM ammonium acetate/acetic acid; the pH 7 buffer used 50 mM ammonium dihydrogenphosphate/ ammonium hydrogenphosphate and for the buffer at pH 9 a 50 mM ammonium acetate/ ammonium hydroxide was used. The conditions of the experiments are presented in Table 2.

Table 2 Experimental conditions

Variables	Levels
Thiosalt	Thiosulfate, Trithionate, Tetrathionate
Temperature (°C)	4, 15, 30
pH	2, 4, 7, 9
Concentration (ppm)	250, 500, 1000
Time	0 to 72 hours
Reagent (mole ratio with thiosalt)	H_2O_2 (3.5)

Batch studies were conducted in the lab using accurately weight amounts of selected thiosalt species dissolved in 100 mL of buffer solution. The contents were transferred to a 250 mL Erlenmeyer flask, sealed with a stopper and agitated at the temperature of study. 1.5-mL aliquots were taken at specific times and filtered using a 0.2 μm nylon filter. The sampling protocol was as follows: filter sample and immediately flash freeze in liquid nitrogen and store at -80 °C until analysis, samples are transferred from the ultralow freezer (-80 °C) to a regular freezer (-4 °C) on the day of analysis and allowed to thaw for 10 minutes only before analysis.

2.2 Analytical Method

Analysis was done using capillary electrophoresis (CE) (Agilent 1602) with UV detection. A 50 μm inner diameter base fused-silica capillary (Microsolv Technology Corporation), 48.5 cm total length and 40 cm effective length was used in all analyses. The capillary was loaded in a cassette and the temperature of the equipment was set at 23°C during experiments. The background electrolyte (BGE) used was was pyromellitic acid (chromophore), hexamethonium bromide (EOF modifier) and Triethanolamine (for pH adjustment) and filtered with a 0.2 μm nylon filter before use. A portion of the sample was placed in a 1-mL polypropylene vial with polyurethane snap cap. The operational procedure for the CE was: flush capillary with 1 M aqueous sodium hydroxide for 15 min, BGE for 10 min, then inject sample hydrodynamically at a pressure of 50 mbar for 10 seconds, carryout separation (capillary zone electrophoresis) at a voltage of 30 kV in negative mode. The capillary was contained in temperature-controlled compartment set at 23°C. The detection wavelengths were 214 nm for thiosulfate and tetrathionate, and 194 nm for trithionate.

2.3 Equilibrium Analysis and Determination of Reaction Rates

Equilibrium simulations and reaction-rate determination were done following the same procedure developed by Miranda-Trevino et al. (2012b). The equilibrium concentrations for thiosalts in the presence of oxidation reagents were calculated with the Gibbs free energy minimization approach using the HSC Chemistry software V7.0. The simulations were done assuming 1 L of solution and a dissolved oxygen concentration of $1x10^{-2}$ M. Thiosalts reactivity is governed predominantly by pH and the presence of oxidizers and to a lesser extent temperature for the range of pond conditions studied (Vongporm, 2008). As such, in these calculations the pH of the solution to be studied was set and the equilibrium analyzed from 4 to 30°C.

3. Results

3.1 Equilibrium Calculations

Equilibrium predicted for thiosalts mixtures and pure species at pH 2 and 4 in the presence of selected reagents are presented in Table 3. Similar to the studies done with pure species; the end products of the calculations can be divided in two groups; acidic or mildly acidic, and neutral or basic. In acidic and mildly acidic conditions (pH 2 and 4), the degradation of thiosalts yields sulfate and elemental sulfur, while neutral and alkaline conditions (pH 7 and 9) yield a mixture of hydrogen sulfide (H_2S) and its ions. Thiosalts oxidation decreases the pH of the solution due to the generation of hydrogen ions; for the simulations done at pH 7 and 9, the pH in the simulation was maintained using buffer compounds; these compounds do not participate in the oxidation of thiosalts. Sulfate and elemental sulfur are expected to form, however, the presence of hydrogen sulfide at alkaline conditions is rarely reported as a sulfur species quantified or detected.

Table 3. Equilibrium Calculation results for single thiosalt species and mixtures

Equilibrium Results as %total sulfur in solution Temperature Range: 4 to 30 °C pH range: 2 to 4			
Reagent in Solution	**Thiosalt**	**SO_4^{2-} (% Sulfur)**	**S^o (% Sulfur)**
Pyrite ($1x10^{-2}$mol) $CuSO_4$ ($1x10^{-2}$mol) $FeSO_4$ ($1x10^{-2}$mol)	Thiosulfate	72	28
	Trithionate	98	2
	Tetrathionate	80	20
	Thiosalt Mix	69	30
H_2O_2 (50% concentration)	Thiosulfate	100	0
	Trithionate	100	0
	Tetrathionate	100	0
	Thiosalt Mix	75	25

As shown in Table 3, in the temperature range studied and under acidic conditions, the end products of thiosalt oxidations are the same: sulfate and elemental sulfur, and their concentrations do not vary with temperature or pH. Nevertheless, the type of reagent present in the simulation does have an impact on the percentage distribution between sulfate and elemental sulfur as a result of different reaction pathways.

On the other hand, simulations done at neutral and alkaline conditions show that the temperature has an effect in the final concentration of sulfur species. In alkaline conditions, the products obtained in the simulation are hydrogen sulfide and bisulfide.The percentage of sulfur as hydrogen sulfide and bisulfide (HS^-) varies according to the temperature from 35% at 4°C to 55% at 30 °C S for hydrogen sulfide at pH 7 to 65% to 75% at pH 9 at the same temperatures. It is notable that the speciation represented by the percentages was dependent on temperature and pH rather than the reagent or thiosalt(s) present in solution. Under acidic conditions, the key factors for the different percentages of sulfur are the type of reagent and the specific thiosalt, though in all instances the mixed systems lead to lower rates of conversion to sulfate than the pure thiosalts for each oxidation treatment, possibly due to interactions between thiosalt species during their oxidation.

3.2 Thiosalt Oxidation by Hydrogen Peroxide

Preliminary experimental results for the oxidation of thiosulfate and trithionate with hydrogen peroxide show that the reactions are likely pH dependent. The results obtained for thiosulfate show that the reaction rate at pH 4 is higher than the reaction rates at pH 2, 7 and 9 (Figure 3). After only 9 minutes of reaction, most of the thiosulfate was converted to tetrathionate at 30°C. This result is unexpected as thiosulfate was not reactive at pH 4 as a pure species. Tetrathionate can be synthesized from thiosulfate in the presence of oxidizing agents such as iodine, especially at low temperatures hence, the reaction pathway is possible. Equilibrium predictions predict that elemental sulfur is an end product of thiosulfate oxidation, but it was not detected in these experiments. However, these experiments were very short (9 minutes) and sulfur formation could occur with longer experimental runs. There is also reactivity at neutral and alkaline pH, which was not observed in the pure species experiments, though both reaction rates are slower than the analogous pure species reaction rates at pH 2. Under alkaline conditions, tetrathionate will undergo oxidation, however without oxidizing reagents, oxidation occurs on a relatively long time scale; thus it follows that longer experiments using the oxidant would yield sulfate as an end product. Further studies should confirm and provided additional information regarding this behavior.

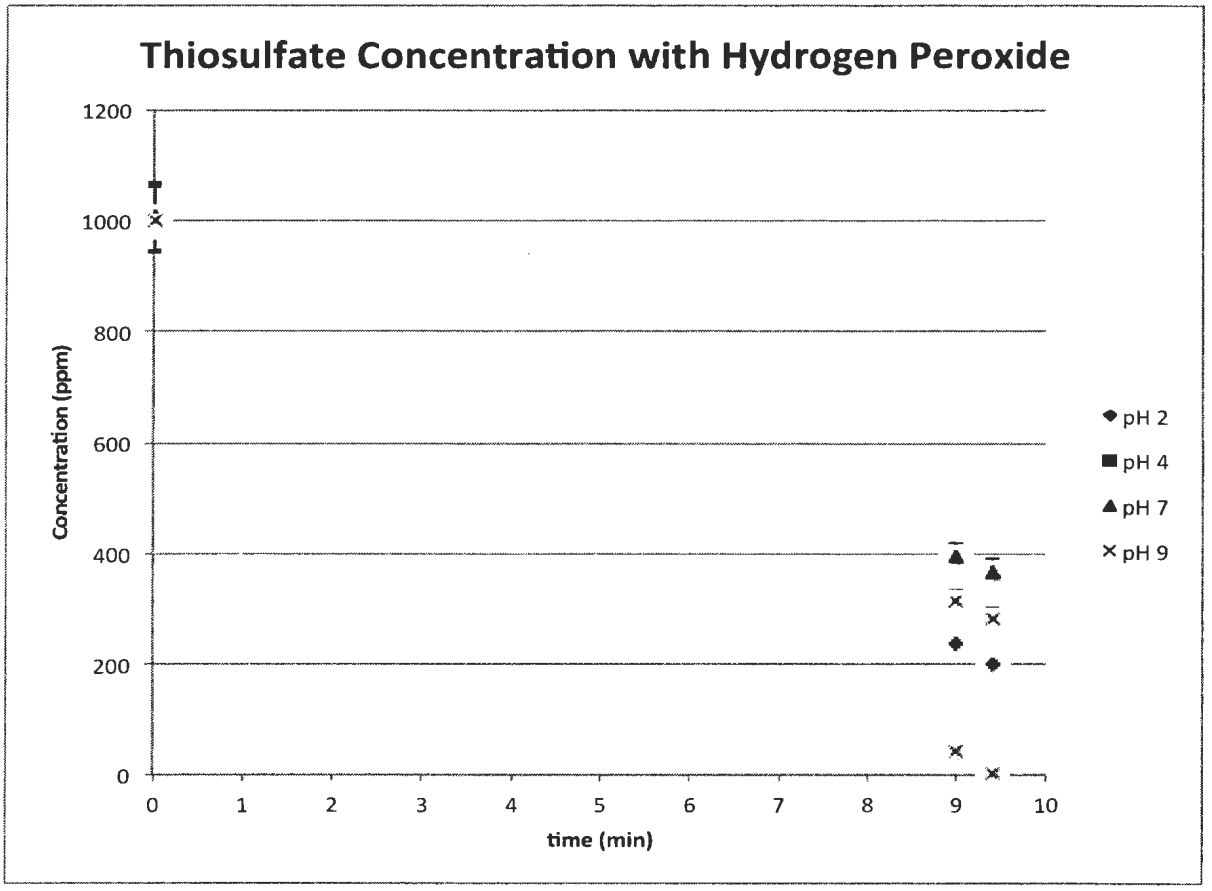

Figure 3. Change in concentration of thiosulfate in the presence of hydrogen peroxide with varied pH

The difference in how the reactions progress with and without hydrogen peroxide is significant. The reaction as pure species takes approximately 6 hours to reach ~60% completion at pH 2 and 30°C, while with the addition of H_2O_2 the reaction progress is ~80% complete in the first 9 minutes. The differences in the products are also noteworthy. Elemental sulfur and hydrogen sulfide are not detected during thiosulfate oxidation with hydrogen peroxide, and sulfate is the main product.

The reaction pathway for thiosulfate oxidation is also affected by the pH of the solution. As shown in Figure 3, the thiosulfate concentration is close to zero after 9 minutes at pH 4, which is lower than the concentration at pH 2. This is unexpected as the pure species studies showed reactivity at pH 2 but not at pH 4. Future studies should include not only

the change of thiosulfate in the presence of hydrogen peroxide but also the products for the oxidation. Sulfur species reaction pathways vary with pH, which could explain the faster reaction rate. Also the oxidation efficiency of hydrogen peroxide at different pH should be evaluated as it could affect the reaction rates.

Preliminary tests for trithionate show that, unlike pure species, the reaction rate of trithionate with hydrogen peroxide is pH dependent (Figure 4). Acidic conditions had slower reaction rates than neutral or alkaline conditions. Results from pure species show that at pH 2 and 4 and 30°C the reaction progress is only 20% complete, which is within the experimental error of trithionate detection. This shows that the effect of the oxidizing reagent on trithionate oxidation is minimal, as has also been suggested by Druschell (2003b).

At neutral and alkaline conditions, hydrogen peroxide does accelerate the trithionate reaction rate to 50 to 60% consumption of trithionate; without the reagent at those same conditions the consumption is only 30%. Comparing the reactivity of thiosulfate and trithionate, the former is more reactive than the latter with hydrogen peroxide at acidic and alkaline conditions. The main product of oxidation of trithionate was tetrathionate, which is one of the key products of the oxidation as a pure species. The other product in the pure species oxidation of trithionate reaction is thiosulfate, but it is likely that the presence of H_2O_2 quickly oxidizes thiosulfate to sulfate.

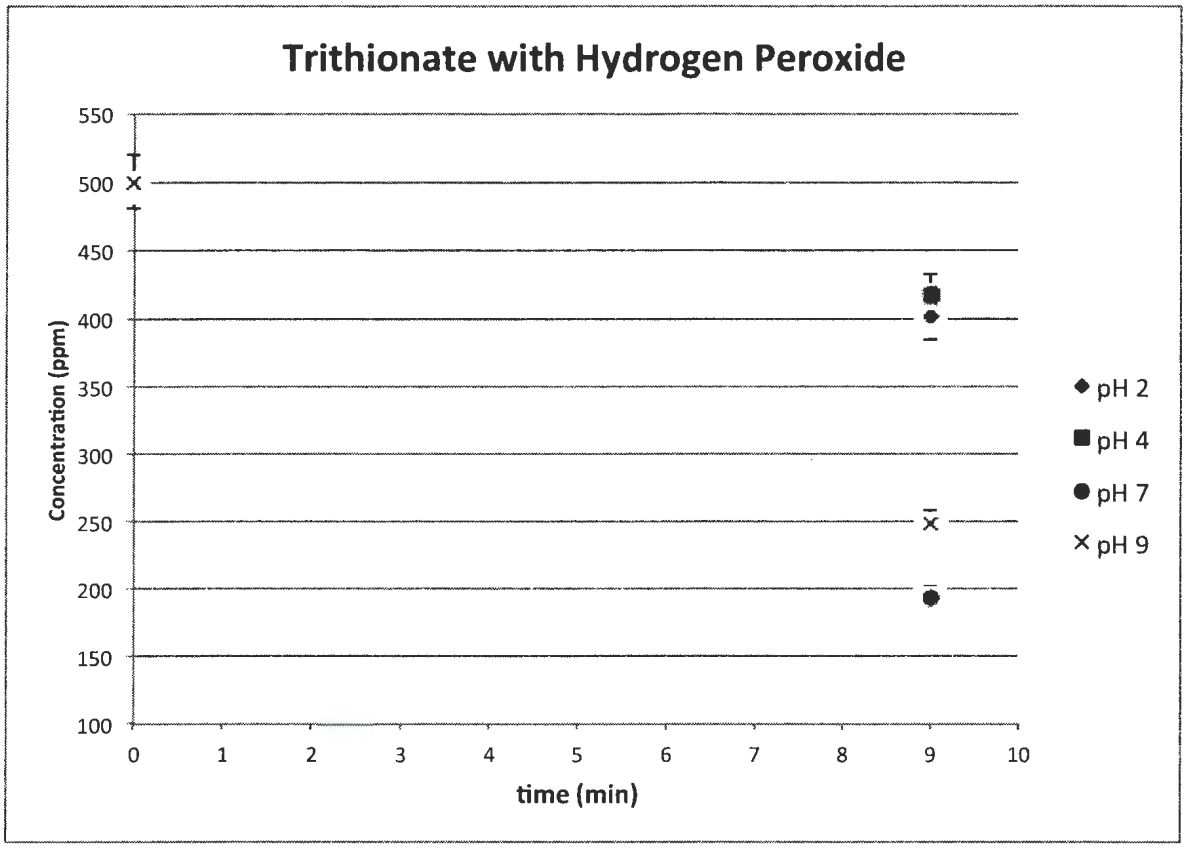

Figure 4. Change in concentration for trithionate in the presence of hydrogen peroxide at different pH

The marked difference in reaction rate emphasizes the need to determine thiosalt speciation during treatment, as the efficiency will depend on the predominant species in solution. Longer experimental runs are required to determine if elemental sulfur is precipitated at acidic conditions, as will be needed for characterization of the other products predicted from the equilibrium calculations.

Equilibrium calculations suggest that bisulfide or sulfide species would be the end product of thiosalt oxidation in neutral and alkaline conditions. The experimental runs for the preliminary tests with hydrogen peroxide were too short to detect the presence of H_2S, bisulfide or sulfide.. However, it is expected that as with the mixtures of thiosalts studied without oxidants for times of 72 hours, species such as sulfate and thiosulfate will accumulateover the longer reaction times. Though time restrictions meant that

hydrogen peroxide and tetrathionate experiments were not possible during the course of this research, a comparison of the results from Voslar et al. (2006) with the results of tetrathionate degradation at pH 9 and 30°C without oxidants shows that decomposition of tetrathionate is extremely fast in the presence of hydrogen peroxide in alkaline media (Figure 5). In contrast, in experiments without hydrogen peroxide no significant change in tetrathionate concentration was measurable over the duration of the Voslar et al. experiment. The products proposed by Voslar et al. (2006) during the oxidation with hydrogen peroxides are the same as those obtained from the pure species experiments, namely sulfate, trithionate and thiosulfate. However, further studies are required to comparison to what Voslar et al. (2006) proposed, as the generation of sulfate in the lab is minimal in comparison to they one proposed. Nevertheless, the presence of peroxide accelerates the same products in both of these systems could indicate that the reaction pathway is the same.

Finally, Table 4 shows the products of thiosalt oxidation in the presence of various reagents proposed by different authors. In general terms, sulfate and tetrathionate will be main products under acidic conditions, while thiosulfate, sulfate and trithionate will be produced under alkaline conditions. Equilibrium calculations provide a reference in terms of the end products for thiosalt oxidation. Under acidic conditions, the equilibrium composition seems to be in agreement with what it is obtained in the lab, as sulfate is one of the main species detected and elemental sulfur could be form under reaction pathways already known. The situation is different for neutral and alkaline solutions where the pathway for the formation of hydrogen sulfide is unknown and not likely to occur during the conditions of the experiments or in the pond due to time constraints.

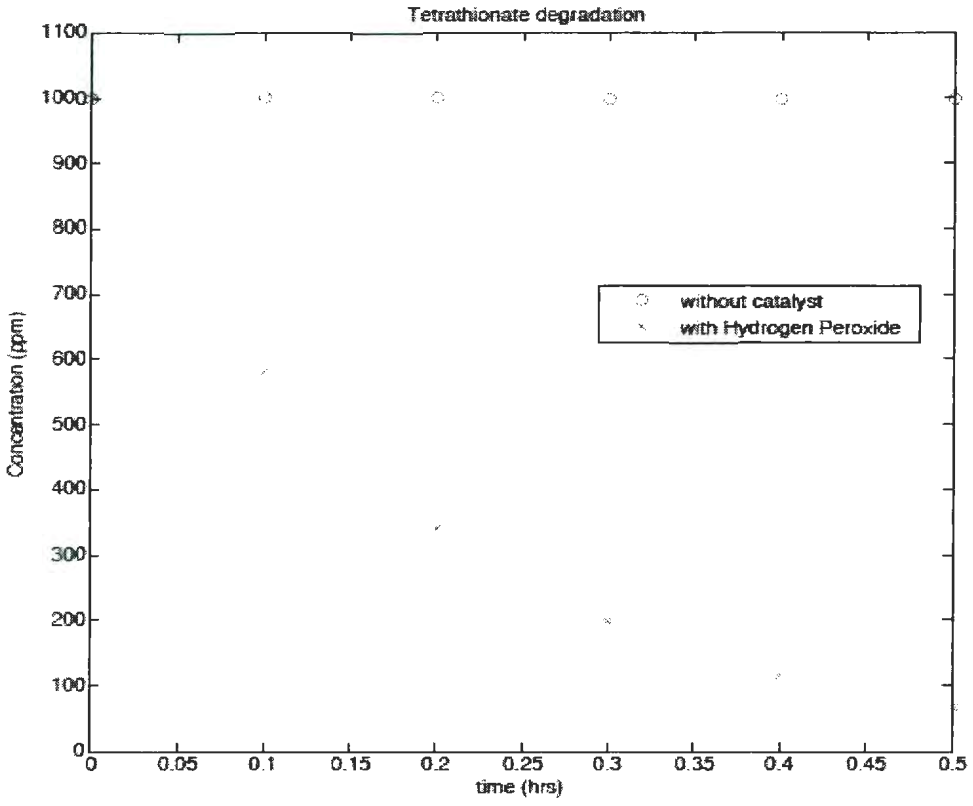

Figure 5. Tetrathionate degradation in the presence of hydrogen peroxide in alkaline conditions

Table 4 Thiosalt products reported by different studies for different reagents and conditions

Thiosalt	**Reagent**	**Conditions**	**Products**		**Reference**
Thiosulfate	H_2O_2	< pH 5	$S_4O_6^{2-}$	100%	Voslar et al. 2006
	FeS_2	Acidic pH	$S_4O_6^{2-}$	100%	Xu and Schoonen 1995
	CuS CuS_2	O_2 saturated	SO_4^{2-} via $S_4O_6^{2-}$	100%	Chanda and Rempel 1987
Trithionate	$OH^{\bullet}$	Acidic pH	SO_4^{2-}	100%	Druschell 2003b
Tetrathionate	$OH^{\bullet}$	Acidic pH	SO_4^{2-}	100%	Druschell 2003b
	H_2O_2	Alkaline pH	SO_4^{2-} $S_2O_3^{2-}$ $S_3O_6^{2-}$	25% 50% 25%	Voslar et al. 2006

4. Conclusions

Thiosalt reactivity in the presence of different catalysts or reagents can vary according to the species and conditions of the pond or solution. This paper presents an overview of initial studies on the oxidation of individual thiosalts with selected reagents for enhanced oxidation that provides the background information required for further studies in the area. During the studies, it has been shown that these reagents affect reaction progress and rate, usually by accelerating oxidation process. In some cases, such as with tetrathionate in alkaline conditions, the product distributions are similar to the ones obtained in pure species studies, but in others, the reagents promote oxidation to sulfate, which is present but not abundant in the pure species studies.

The effect of different reagents on specific species requires more attention in future studies. For example, Druschell (2003b) studied the reaction of tetrathionate and trithionate with the hydroxyl radical ($OH^{\bullet}$) and concluded that the reaction was too fast to follow with traditional analytical methods. Thiosulfate was not included in their experimentshowever; further studies should include it to determine its reaction rate in the presence of hydroxyl radical, especially in alkaline solutions, as those are the traditional operational conditions for thiosalt treatment (Fedath, 2010). Deserving further attention are conditions in which the reagent does not enhance oxidation of thiosalts species, as seen for trithionate and tetrathionate under acidic conditions in the presence of hydrogen peroxide (Druschell, 2003b).

Pyrite plays an important role in the oxidation of thiosulfate; however, further studies should include the reactions of trithionate with this mineral at different pH conditions, particularly since this species is the only sulfur species able to react over a wide range of pH.

Copper (between 30- 60°C) and iron act as catalysts to enhance the oxidation of thiosalts by hydrogen peroxide. The challenge for both metals is to study their effects at

different pH environments for the three major species (individually and in mixtures) to understand the interactions and potential reaction pathways.

An important catalyst in thiosalt oxidation not discussed here are bacteria. A brief summary of the key types and their effects on thiosalts can be found in Miranda-Trevino et al. (2012a). A key aspect for studies going forward is the interaction of microorganisms with trithionate and the potential pathways and products under different conditions. One of the key challenges while working with microorganisms is that the bacteria adapt to different environmental conditions, so the most useful data for any given system (receiving waters, etc.) will use bacteria isolated from that system and this should be considered when devising the study.

Finally, the end product of these studies should be the reaction rates for the different thiosalts species under different conditions; this will be key to improving the modeling of treatment options and environmental risk assessment studies.

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Summary

Thiosalts have been identified as key precursor in the generation of acid mine drainage. The research work presented in this thesis aims to provide a better understanding of the reaction rates of the three main thiosalt species (thiosulfate, trithionate and tetrathionate) under different conditions of temperature and pH and in the presence of different catalysts; develop a model to predict thiosalt behavior in the ponds and evaluate thiosalt treatments and environmental risks associated with the compounds.

The research has been divided into four parts: The first objective was to present an in-depth review of the information published about thiosalts, with an emphasis on analytical tools, kinetic studies and a brief overview of the treatment options available. The resulting paper in addition to be the first of its kind in the last 25 years, provided the background for the next stages of the research. A key for the review paper was to evaluate the temperature and pH conditions from previous studies to determine whetherthe typical pond conditions had been extensively studied before. The result of this evaluation was that there was a significant gap in terms of thiosalt kinetic studies at the conditions proposed for the research, which represent the most likely conditions found in the pond.

After establishing the theoretical background and summarizing relevant thiosalt information in the first chapter, the second goal was to carry out the studies to develop an understanding of the reaction rates for the individuals thiosalts (thiosulfate, trithionate and tetrathionate) over a temperature range of 4-30 ℃ and pH of 2 to 9. The studies were performed with the pure species under controlled conditions in the lab. Key contributions resulting from the work here included: identification the reactive conditions for each thiosalts; establishment of the relevance of thiosalt speciation in the study and calculation of reaction rates for each of the thiosalts as a function of temperature and pH.

Due to the complexity of the study, the gathering and analysis of kinetic data were key components of the research. The system used was a batch reactor with set conditions of temperature, pH, type of thiosalt and concentration. An specific reaction constant (k) and reaction order (n) could be obtained for each set of data, but the challenge was to be able to find a reaction constant (as a function of temperature) and order that could be used across the different conditions for each thiosalt. Therefore, the optimization routine used in the research consisted on two-steps sequence. The first part obtained the kinetic information (k and n) for each set of data and the second step optimized those values for the whole range of data for the specific species. Since the experiments were conducted in buffer solutions, it was possible to extract the hydrogen ions concentration from the reaction constant. In addition, an Arrhenius plot provided k as a function of temperature. This approach yielded the possibility to present reaction rates as function of temperature and pH.

For mixtures, the optimization approach was the same; however, the conceptual model involved the decoupling of reactions in solution. By decoupling the reactions, it was possible to use the reaction rates obtained by the pure species and added them as a term in the mixture equation. Since the reaction constant and order is already know for the pure species rate, the system maintains only two unknowns (k and n of the decoupling section).

After studying the behavior of the single thiosalt species in solution, the effort involved the study of the behavior of thiosalt mixtures under the same conditions. This is a logical step in the progression of the research as thiosalt generation in the mining process and in tailing ponds is most likely to result in a mixture rather than a single species, hence the importance of understanding how it will react. One of the objectives in this part of the research was to apply a decoupling approach to the mixture reaction rates with the information provided by the pure species studies.

The thiosalt mixture experiments were conducted at different temperatures and pH, however the reaction rates presented are specific of the pH and temperatures conditions where they were calculated. In other words, additional studies will need to be conducted to calculate the reaction rates of mixtures as a function of temperature and pH. This work provided useful information on the interaction between the different species to propose the global reaction pathways.

After studying the reaction rates for thiosalt under controlled conditions as a pure species and in mixture, the next step is to expand the studies in the presence of reagents. The first chapter of the thesis presents an overview of reagents and their effects on specific thiosalt species. However, there is the need to expand on the work of those previous studies in terms of pH and temperature conditions, reagents and thiosalt species present. The final section of the thesis presents preliminary results of thiosalt studies in the presence of selected reagents and analyzes the gaps present in the current work. The results presented in section four could be used as starting point for future thiosalt research with reagents. The work presented here provides valuable information regarding the behavior of thiosulfate, trithionate and tetrathionate in solutions, proposes reaction rates as function of temperature and pH and provides with global reaction pathways for each of the species at different conditions.

Pyrite is a known precursor of thiosalts and the behavior of thiosulfate in its presence has been documented before (Xu and Schoonen, 1995). However, due to the process conditions, other thiosalt species such as trithionate and tetrathionate could be dissolved in solution, hence, it will be important to understand their behavior and reaction pathways in the presence of pyrite.

Thiosalt treatment with hydrogen peroxide and ferric sulfate is a common practice in the mining industry. Preliminary test show that the efficiency of this treatment could depend on the predominant thiosalt species present in solution

as well as the temperature and pH conditions. Future studies should provide more insight regarding the reaction rates of singles species at typical treatment conditions and also the behavior of thiosalt mixtures in those same conditions.

Trithionate is a species that should be studied in more detail. The studies done in the current research shows that it is the only species that is reactive in both acidic and alkaline conditions and the reaction rate is independent of pH. Understanding the reaction pathways and its behavior in the presence of reagents such as hydrogen peroxide and microorganisms is important.

One of the key challenges in the mining industry is the sulfur management. The results presented indicates that the various oxidation states and interactions between species could have a negative effect on the process efficiency, but also could generate problems such as scaling and acid mine drainage.

Insight into the behavior and reaction rates of the main thiosalt species will help in closing the sulfur balance in the mining process. Once it is understood how the sulfur is changing along the process, it will be possible to improve the efficiency of the treatment and minimize negative effects of sulfur compounds on the environment.

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Appendices

Note: Empty spaces in the data means that the compound was not analyzed and zero means that it was not detected.

A.1 Thiosalt Data from pure species

Thiosalt	Tetrathionate					
Initial Concentration	250					
pH	Temperature (°C)	Rxn Time	Thiosulphate (ppm)	Trithionate (ppm)	Tetrathionate (ppm)	Sulphate (ppm)
2	4	0	0	3	250	not analyzed
		24	0	3	259	not analyzed
		30	0	2	251	not analyzed
		48	0	3	247	not analyzed
		72	0	3	252	not analyzed
	15	0	0	0	250	not analyzed
		6	0	0	250	not analyzed
		24	0	0	256	not analyzed
		30	0	0	260	not analyzed
		48	0	0	250	not analyzed
		72	0	0	249	not analyzed
	30	0	0	2	250	not analyzed
		6	0	1	254	not analyzed
		24	0	0	254	not analyzed
		30	1	0	253	not analyzed
		48	0	0	244	not analyzed
		72	0	0	249	not analyzed
4	4	0	0	0	250	not analyzed
		24	0	2	255	not analyzed
		30	0	2	253	not analyzed
		48	0	2	251	not analyzed
		72	0	4	249	not analyzed
	15	0	0	0	250	not analyzed
		6	0	1	254	not analyzed
		24	0	0	255	not analyzed
		30	0	1	247	not analyzed
		48	0	3	241	not analyzed
		72	0	0	245	not analyzed
	30	0	0	1	250	not analyzed
		6	0	1	248	not analyzed
		24	0	1	243	not analyzed
		30	0	0	243	not analyzed
		48	0	0	246	not analyzed
		72	0	0	246	not analyzed
7	4	0	0	0	250	0
		24	0	0	245	0
		48	0	0	250	0
		72	0	0	247	0
	15	0	0	0	250	not analyzed
		6	0	0	247	not analyzed
		24	0	1	246	not analyzed
		30	0	1	246	not analyzed
		48	0	1	237	not analyzed
		72	0	3	248	not analyzed
	30	0	0	2	250	not analyzed
		30	0	4	250	not analyzed
		48	6	3	255	not analyzed
		72	1	3	251	not analyzed
9	4	0	1	5	250	0
		24	10	9	237	0
		48	12	10	227	0
		72	13	8	225	0
	15	0	0	3	250	0
		3.5	2	4	247	
		7	3	3	260	
		24	9	5	238	0
		30	10	5	235	
		48	12	5	228	0
		72	13	7	221	0
	30	0	0	0	250	0
		7	13	4	239	
		24	25	14	224	0
		30	32	16	225	
		48	33	24	222	2
		72	43	32	210	5

Thiosalt	Tetrathionate					
Initial Concentration	500					
pH	Temperature (°C)	Rxn Time	Thiosulphate (ppm)	Trithionate (ppm)	Tetrathionate (ppm)	Sulphate (ppm)
		0	0	0	500	0
		24	0	2	501	0
		48	0	0	503	0
	4	72	0	8	488	0
		0	0	7	500	
		24	0	2	499	
		30	0	2	505	
		48	0	3	519	
	15	72	0	3	523	
		0	0	2	500	
		6	0	3	493	
		24	0	3	505	
		30	0	3	496	
		48	0	2	503	
2	30	72	0	2	503	
		0	0	0	500	
		24	0	0	496	
		48	0	0	501	
	4	72	0	0	501	
		0	0	3	500	
		24	0	2	495	
		30	0	3	511	
		48	0	2	506	
	15	72	0	2	508	
		0	1	3	500	
		24	2	1	495	
		48	3	1	505	
4	30	72	2	0	492	
		0	0	0	500	0
		24	0	0	502	0
		48	0	0	491	0
	4	72	0	0	491	0
		0	2	4	500	
		6	1	2	501	
		24	0	2	499	
		30	0	4	497	
		48	3	2	507	
	15	72	1	2	519	
		0	0	2	500	0
		6	0	0	501	
		24	0	4	500	0
		30	0	3	504	
		48	3	2	498	0
7	30	72	2	3	476	0
		0	4	3	500	0
		6	6	6	491	
		24	13	9	469	0
		48	19	11	459	0
	4	72	22	11	458	0
		0	0	2	500	0
		3.5	4	3	487	
		7	6	3	505	
		24	17	6	485	0
		48	20	10	462	0
	15	72	24	14	459	0
		0	3	4	500	0
		6	34	16	429	
		24	57	40	381	0
		48	82	69	330	0
		72	104	86	281	8
9	30	96	125	104	243	11

Thiosalt	Tetrathionate					
Initial Concentration	1000					
pH	Temperature (°C)	Rxn Time	Thiosulphate (ppm)	Trithionate (ppm)	Tetrathionate (ppm)	Sulphate (ppm)
		0	0	6	1000	
		24	0	3	1039	
		30	0	2	995	
		48	0	2	985	
	4	72	0	1	997	
		0	1	2	1000	
		24	0	2	1002	
		48	1	3	1016	
	15	72	3	2	1006	
		0	1	2	1000	
		24	1	2	1004	
		48	2	3	1003	
2	30	72	2	3	1010	
		0	0	4	1000	
		24	0	6	1013	
		30	0	4	997	
		48	0	4	1029	
	4	72	0	2	997	
		0	1	3	1000	0
		24	2	4	997	0
		48	0	2	994	0
	15	72	0	6	951	25
		0	1	2	1000	
		24	3	3	1007	
		48	2	2	993	
4	30	72	3	2	995	
		0	0	2	1000	
		24	0	6	983	
		30	0	3	955	
		48	0	4	972	
	4	72	0	3	991	
		0	0	2	1000	
		24	2	4	998	
		48	2	4	996	
	15	72	0	4	999	
		0	0	1	1000	
		6	1	3	986	
		24	3	3	986	
		30	2	0	994	
		48	5	6	1035	
7	30	72	4	10	996	
		0	6	5	1000	0
		6	10	7	999	
		24	29	14	947	0
		48	35	25	927	0
	4	72	34	49	906	0
		0	2	4	1000	0
		3.5	8	6	981	
		7	14	9	967	
		24	28	13	993	2
		30	29	14	970	
		48	33	23	970	3
	15	72	38	29	946	5
		0	6	6	1000	0
		6	59	25	909	0
		24	99	76	788	0
		30	117	88	764	0
		48	166	131	707	8
		72	229	178	599	14
9	30	96	262	188	463	21

Thiosalt	Trithionate					
Initial Concentration	250					
pH	Temperature (°C)	Rxn Time	Thiosulphate (ppm)	Trithionate (ppm)	Tetrathionate (ppm)	Sulphate (ppm)
		0	0	250	0	
		24	0	254	0	
		30	2	248	0	
		48	2	249	0	
	4	72	3	248	0	
		0	0	250	1	
		6	0	248	0	
		24	2	245	1	
		30	2	249	0	
		48	3	243	1	
	15	72	4	245	1	0
		0	0	250	1	
		6	0	247	1	10
		24	8	244	2	19
		48	11	233	1	23
2	30	72	12	209	0	0
		0	0	250	0	0
		24	0	250	0	
		30	0	246	0	0
		48	3	244	0	0
	4	72	2	244	0	0
		0	0	250	0	
		6	0	243	0	0
		24	3	236	0	
		30	3	232	0	0
		48	5	239	1	15
	15	72	6	229	0	0
		0	0	250	1	
		6	3	245	1	13
		24	13	222	0	24
		48	23	203	1	37
4	30	72	36	189	0	
		0	0	250	0	
		24	0	248	0	
		48	0	248	0	
	4	72	0	243	0	0
		0	0	250	0	
		6	0	250	0	0
		24	3	242	0	
		30	4	241	0	0
		48	5	242	0	0
	15	72	8	231	0	0
		0	0	250	0	
		6	4	245	0	10
		24	15	237	1	
		30	19	222	1	26
		48	43	207	2	35
7	30	72	38	188	0	
		0	0	250	0	
		24	0	254	0	
		48	2	254	0	
	4	72	2	257	0	8.73
		0	0	250	0	8.75
		3.5	0	248	0	8.73
		7	0	248	0	8.74
		24	0	259	0	8.72
		30	5	256	0	8.71
		48	7	256	0	8.72
	15	72	8	251	0	0
		0	0	250	1	
		7	4	243	5	12
		24	13	238	2	29
		48	20	234	4	42
9	30	72	16	216	0	

Thiosalt	Trithionate					
Initial Concentration	500					
pH	Temperature (°C)	Rxn Time	Thiosulphate (ppm)	Trithionate (ppm)	Tetrathionate (ppm)	Sulphate (ppm)
		0	0	500	0	
		6	0	506	0	
		48	0	504	0	
	4	72	3	502	1	0
		0	0	500	1	8
		24	0	501	2	
		30	4	502	4	10
		48	3	472	4	18
	15	72	4	480	1	0
		0	0	500	0	
		6	4	490	1	11
		24	13	468	3	26
		48	17	435	4	36
2	30	72	19	419	0	14
		0	0	500	0	11
		24	0	491	0	8
		48	2	496	0	12
	4	72	3	490	6	0
		0	0	500	7	0
		24	4	500	8	
		30	5	491	3	6
		48	8	495	3	15
	15	72	13	485	1	0
		0	0	500	2	
		6	7	481	1	27
		24	24	453	1	
		30	29	436	2	48
		48	45	406	4	74
4	30	72	67	379	0	
		0	0	500	0	
		24	0	500	0	
		48	1	500	0	
	4	72	3	494	0	0
		0	0	500	0	
		6	0	494	1	0
		24	5	504	1	0
		48	10	483	2	14
	15	72	14	471	0	0
		0	0	500	1	
		6	8	491	2	28
		24	31	481	2	
		30	39	476	3	50
		48	56	410	6	71
7	30	72	79	371	0	0
		0	0	500	0	0
		24	0	501	0	0
		48	0	491	0	0
	4	72	0	482	0	
		0	0	500	0	
		3.5	0	508	0	
		7	0	507	0	
		24	5	528	0	
		48	11	510	0	
	15	72	15	506	0	0
		0	0	500	2	
		7	6	490	6	0
		24	23	494	7	
		30	27	486	7	55
		48	30	472	6	88
9	30	72	34	442	0	0

Thiosalt	Trithionate					
Initial Concentration	1000					
pH	Temperature (°C)	Rxn Time	Thiosulphate (ppm)	Trithionate (ppm)	Tetrathionate (ppm)	Sulphate (ppm)
		0	0	1000	1	0
		24	1	997	1	
		30	1	999	1	11
		48	2	995	0	12
	4	72	4	989	0	0
		0	0	1000	1	11
		24	6	990	3	13
		48	11	986	15	21
	15	72	8	965	0	10
		0	0	1000	2	16
		6	8	930	5	35
		24	22	917	10	57
		48	35	864	10	72
2	30	72	40	806	0	0
		0	0	1000	1	10
		24	2	1010	1	
		30	3	1009	0	13
		48	4	970	0	22
	4	72	6	991	0	0
		0	0	1000	0	14
		24	10	998	1	17
		48	19	983	2	21
	15	72	29	955	0	0
		0	0	1000	0	18
		6	13	977	2	53
		24	58	903	4	99
		48	101	806	7	135
4	30	72	149	752	0	0
		0	0	1000	1	0
		24	2	975	1	
		30	3	993	2	0
		48	4	1004	1	0
	4	72	7	990	0	0
		0	0	1000	2	
		6	4	997	1	14
		24	10	950	1	31
		48	20	943	2	24
	15	72	31	924	0	0
		0	3	1000	1	9
		6	19	965	3	53
		24	59	898	3	
		30	74	886	7	101
		48	112	825	16	142
7	30	72	147	743	1	0
		0	1	1000	0	
		6	2	995	0	0
		25	1	990	0	
		30	1	988	0	12
		48	3	966	0	18
	4	72	4	964	0	0
		0	2	1000	0	16
		24	11	986	4	21
		48	21	937	2	32
	15	72	30	953	5	0
		0	14	1000	1	23
		7	17	984	3	58
		24	45	962	3	108
		48	76	926	8	168
9	30	72	103	858	0	0

Thiosalt	Thiosulfate					
Initial Concentration	250					
pH	Temperature (°C)	Rxn Time	Thiosulphate (ppm)	Trithionate (ppm)	Tetrathionate (ppm)	Sulphate (ppm)
		0	250	0	0	0
		6	231	0	0	0
		9	218	2	0	6
		24	200	3	0	0
		30	193	3	0	9
		48	174	12	0	17
	4	72	157	14	11	0
		0	250	0	6	0
		3	226	1	4	0
		6	201	0	3	0
		9	185	7	12	0
		24	125	3	16	13
		48	98	2	23	13
	15	72	74	4	12	0
		0	250	3	4	0
		3	200	5	7	0
		6	159	8	5	0
		9	134	7	14	10
		24	81	9	23	11
		48	53	9	33	21
2	30	72	42	11	0	
		0	250	0	0	
		6	253	0	0	
		24	253	0	0	
		30	256	0	0	
		48	256	0	0	
	4	72	249	2	0	
		0	250	0	0	
		6	243	0	0	
		24	243	0	0	
		48	242	5	1	
	15	72	239	0	0	3.94
		0	250	0	1	3.86
		24	250	0	1	3.85
		48	248	2	1	3.83
4	30	72	247	5	1	
		0	250	0	0	
		24	251	3	0	
		48	258	3	0	
	4	72	253	0	0	
		0	250	0	0	
		6	247	0	0	
		30	244	0	2	
		48	251	1	1	
	15	72	273	0	0	
		0	250	0	3	
		6	255	0	3	
		24	242	0	5	
		30	248	0	8	
		48	246	0	13	
7	30	72	242	0	21	
		0	250	9	11	
		30	268	3	22	
	4	72	254	7	6	
		0	250	2	5	
		3.5	251	1	5	
		7	251	0	0	
		24	259	5	13	
		48	259	10	13	
	15	72	256	15	12	0
		0	250	5	11	
		6	249	8	11	18
		24	192	42	5	43
		48	160	79	7	69
		72	104	121	4	106
9	30	96	82	137	8	0

Thiosalt	Thiosulfate					
Initial Concentration	500					
pH	Temperature (°C)	Rxn Time	Thiosulphate (ppm)	Trithionate (ppm)	Tetrathionate (ppm)	Sulphate (ppm)
		0	500	2	2	
		9	454	5	1	17
		24	393	14	5	21
		48	341	14	5	22
	4	72	310	22	5	0
		0	500	0	3	
		1	476	0	4	
		3	422	8	4	
		6	356	2	1	0
		9	327	8	16	15
		24	213	10	28	22
		48	163	18	35	23
	15	72	141	21	3	0
		0	500	1	6	
		1	433	3	3	
		3	307	7	1	
		6	248	15	1	8
		9	210	18	8	20
		24	127	33	23	25
		48	100	35	35	33
2	30	72	91	36	1	
		0	500	1	2	
		24	504	3	1	
		48	481	0	2	
	4	72	496	0	3	
		0	500	0	3	
		24	500	2	4	
		48	497	1	3	
	15	72	497	0	6	0
		0	500	0	3	0
		24	505	5	3	0
		48	502	2	11	0
4	30	72	477	7	2	
		0	500	0	1	
		24	496	0	1	
		48	504	0	2	
	4	72	500	0	1	
		0	500	0	2	
		30	512	0	1	
		48	507	11	3	
	15	72	497	0	0	
		0	500	0	2	
		24	525	0	4	
		48	501	0	7	
7	30	72	506	2	17	0
		0	500	2	7	
		6	509	0	12	0
		30	495	2	10	0
		48	503	2	31	0
	4	72	474	8	16	0
		0	500	3	23	0
		24	480	8	9	0
		48	495	8	13	0
	15	72	479	14	19	0
		0	500	5	27	
		6	483	11	24	6
		24	456	29	21	12
		48	436	48	13	16
		72	429	66	7	26
9	30	96	429	86	0	10

Thiosalt	Thiosulfate					
Initial Concentration	1000					
pH	Temperature (°C)	Rxn Time	Thiosulphate (ppm)	Trithionate (ppm)	Tetrathionate (ppm)	Sulphate (ppm)
		0	1000	3	0	
		3	892	47	0	
		6	866	23	0	11
		9	816	19	0	19
		24	646	31	0	40
		48	609	56	0	46
	4	72	579	79	4	0
		0	1000	0	3	
		1	861	1	6	
		3	738	5	1	
		6	615	20	5	15
		9	540	25	8	35
		24	397	62	26	56
		48	343	89	37	67
	15	72	319	104	5	0
		0	1000	1	2	0
		1	752	7	1	0
		3	507	28	1	0
		6	385	45	1	20
		9	330	56	2	41
		24	262	96	13	56
		48	244	125	23	59
2	30	72	220	131	0	
		0	1000	0	1	
		24	979	0	1	
		48	999	0	0	
	4	72	1002	0	0	0
		0	1000	0	0	11
		24	989	2	1	20
		48	991	3	2	25
	15	72	989	3	1	3.97
		0	1000	5	1	3.87
		6	1010	9	2	3.88
		24	981	8	1	3.86
		30	1019	0	1	3.86
		48	1009	2	2	3.86
4	30	72	992	3	0	
		0	1000	0	1	
		24	983	2	1	
		48	1000	0	0	
	4	72	1033	0	0	
		0	1000	2	1	
		24	1017	0	2	
		48	1011	3	4	
	15	72	1013	2	0	
		0	1000	0	3	
		6	1002	0	5	
		24	981	12	3	
		30	981	10	5	
		48	994	0	9	
7	30	72	1023	3	13	
		0	1000	6	7	
		30	1007	0	22	
	4	72	995	6	20	0
		0	1000	5	22	0
		24	993	7	13	0
		48	1007	14	20	0
	15	72	983	17	17	0
		0	1000	3	23	
		6	987	8	14	4
		24	960	15	20	4
		48	960	29	24	6
		72	927	39	27	8
9	30	96	927	45		

A.2 Results for the initial simulation using RK4 technique.

Thiosulfate (@pH2)

Temperature (℃)	Initial Concentration (mg/L)	K (1/h)	N
4	250	2.6e-03	1.2e+00
	500	3.0e-03	1.2e+00
	1000	2.8e-03	1.2e+00
15	250	3.0e-03	1.4e+00
	500	3.1e-03	1.4e+00
	1000	2.9e-03	1.4e+00
30	250	2.6e-03	1.6e+00
	500	2.6e-03	1.6e+00
	1000	2.3e-03	1.6e+00

Trithionate (@Temp=30℃)

pH	Initial Concentration (mg/L)	K (1/h)	N
2	250	2.0e-03	1.0e+00
	500	2.6e-03	1.0e+00
	1000	3.1e-03	1.0e+00
4	250	4.1e-03	1.0e+00
	500	4.0e-03	1.0e+00
	1000	4.2e-03	1.0e+00
7	250	3.8e-03	1.0e+00
	500	3.9e-03	1.0e+00
	1000	4.1e-03	1.0e+00

9	250	2.0e-03	1.0e+00
	500	5.0e-03	08.0e-01
	1000	2.0e-03	1.0e+00

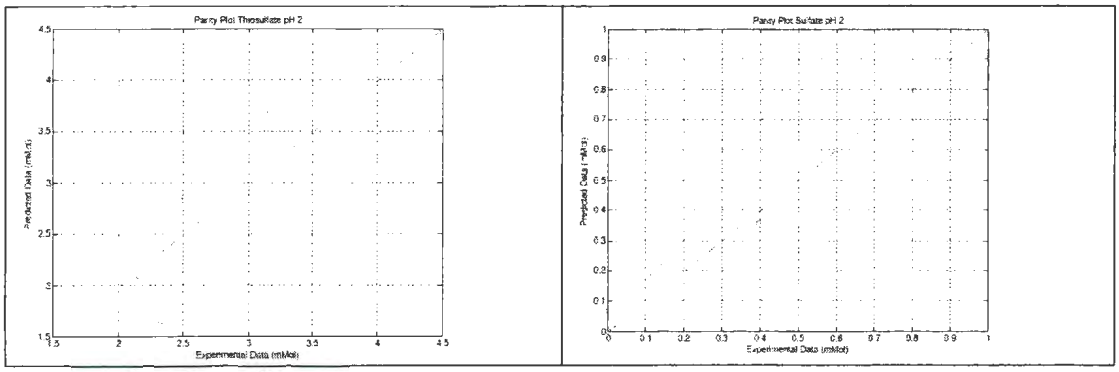
Tetrathionate (@pH9)

Temperature (℃)	Initial Concentration (mg/L)	K (1/h)	N
4	250	1.7e-03	1.0e+00
	500	1.5e-03	1.0e+00
	1000	1.0e-04	1.4e+00
15	250	2.0e-04	1.4e+00
	500	4.6e-03	08.0e-01
	1000	2.8e-03	08.0e-01
30	250	1.0e-04	1.6e+00
	500	8.0e-04	1.4e+00
	1000	5.0e-04	1.4e+00

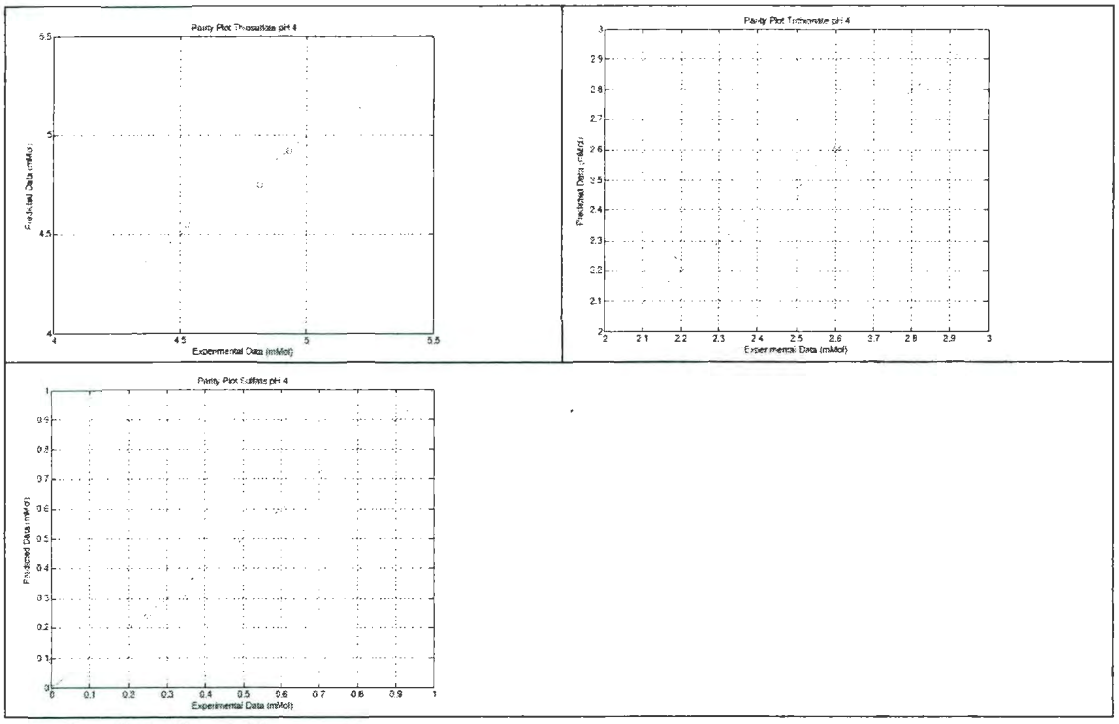
A.3 Pure species reaction rates

pH	Initial Sulfur Species	Reaction Rates
2	$S_2O_3^{2-}$	$-\frac{d[S_2O_3^{-2}]}{dt} = 2.6x10^{-2}\frac{1}{mM*h}[S_2O_3^{-2}]^2$ $\frac{d[S_3O_6^{-2}]}{dt} = 1.2x10^{-2}\frac{mM}{h}$ $\frac{d[SO_4^{-2}]}{dt} = 1.0x10^{-2}\frac{mM}{h}$
	$S_3O_6^{2-}$	$\frac{d[S_2O_3^{-2}]}{dt} = 5.7x10^{-3}\frac{mM}{h}$ $-\frac{d[S_3O_6^{-2}]}{dt} = 3.2x10^{-3}\frac{1}{h}[S_3O_6^{-2}]$ $\frac{d[SO_4^{-2}]}{dt} = 9.5x10^{-3}\frac{mM}{h}$
4	$S_3O_6^{2-}$	$\frac{d[S_2O_3^{-2}]}{dt} = 1.9x10^{-2}\frac{mM}{h}$ $-\frac{d[S_3O_6^{-2}]}{dt} = 4.2x10^{-3}\frac{1}{h}[S_3O_6^{-2}]$ $\frac{d[SO_4^{-2}]}{dt} = 2.0x10^{-2}\frac{mM}{h}$
7	$S_3O_6^{2-}$	$\frac{d[S_2O_3^{-2}]}{dt} = 1.9x10^{-2}\frac{mM}{h}$ $-\frac{d[S_3O_6^{-2}]}{dt} = 4.1x10^{-3}\frac{1}{h}[S_3O_6^{-2}]$ $\frac{d[SO_4^{-2}]}{dt} = 2.1x10^{-2}\frac{mM}{h}$
9	$S_4O_6^{2-}$	$\frac{d[S_2O_3^{-2}]}{dt} = 2.7x10^{-2}\frac{mM}{h}$ $\frac{d[S_3O_6^{-2}]}{dt} = 1.1x10^{-2}\frac{mM}{h}$ $-\frac{d[S_4O_6^{-2}]}{dt} = 7.9x10^{-3}\frac{1}{h}[S_4O_6^{-2}]$ $\frac{d[SO_4^{-2}]}{dt} = 1.9x10^{-3}\frac{mM}{h}$
	$S_3O_6^{2-}$	$\frac{d[S_2O_3^{-2}]}{dt} = 1.1x10^{-2}\frac{mM}{h}$ $-\frac{d[S_3O_6^{-2}]}{dt} = -1.9x10^{-3}\frac{1}{mM*h}[S_3O_6^{-2}]$ $\frac{d[SO_4^{-2}]}{dt} = 2.4x10^{-2}\frac{mM}{h}$

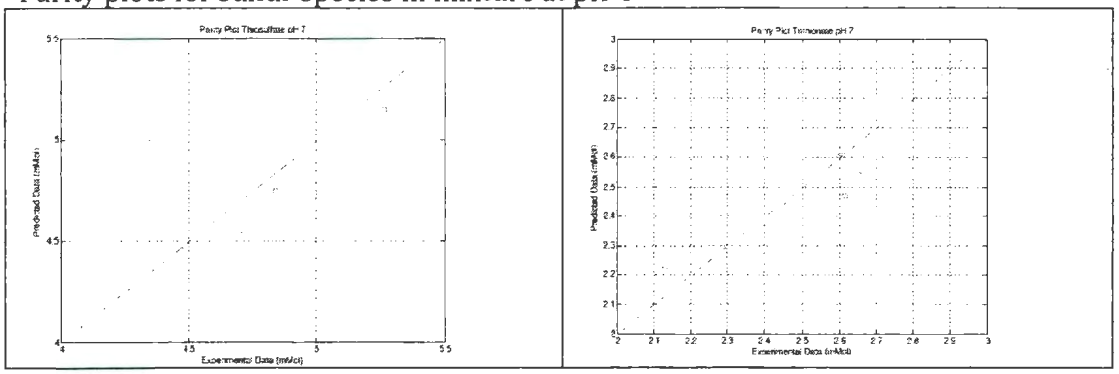
A.4 Parity Plots for Thiosalt mixtures

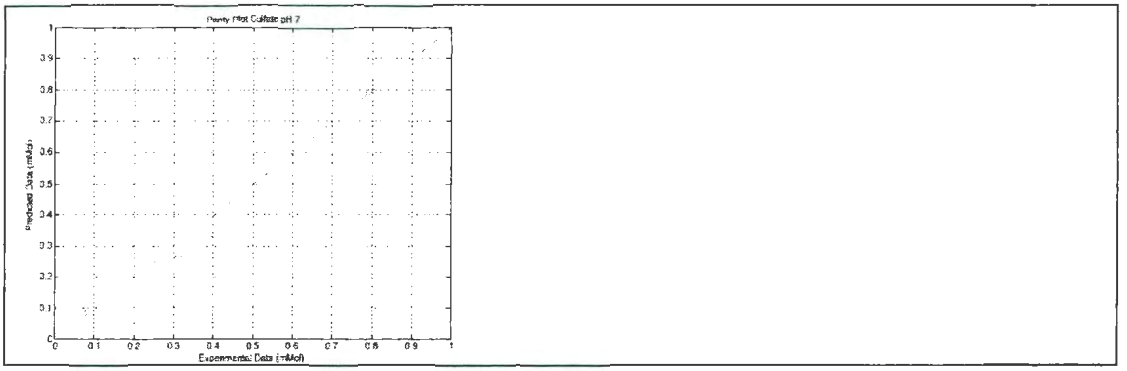


Parity plots for sulfur species in mixture at pH 2

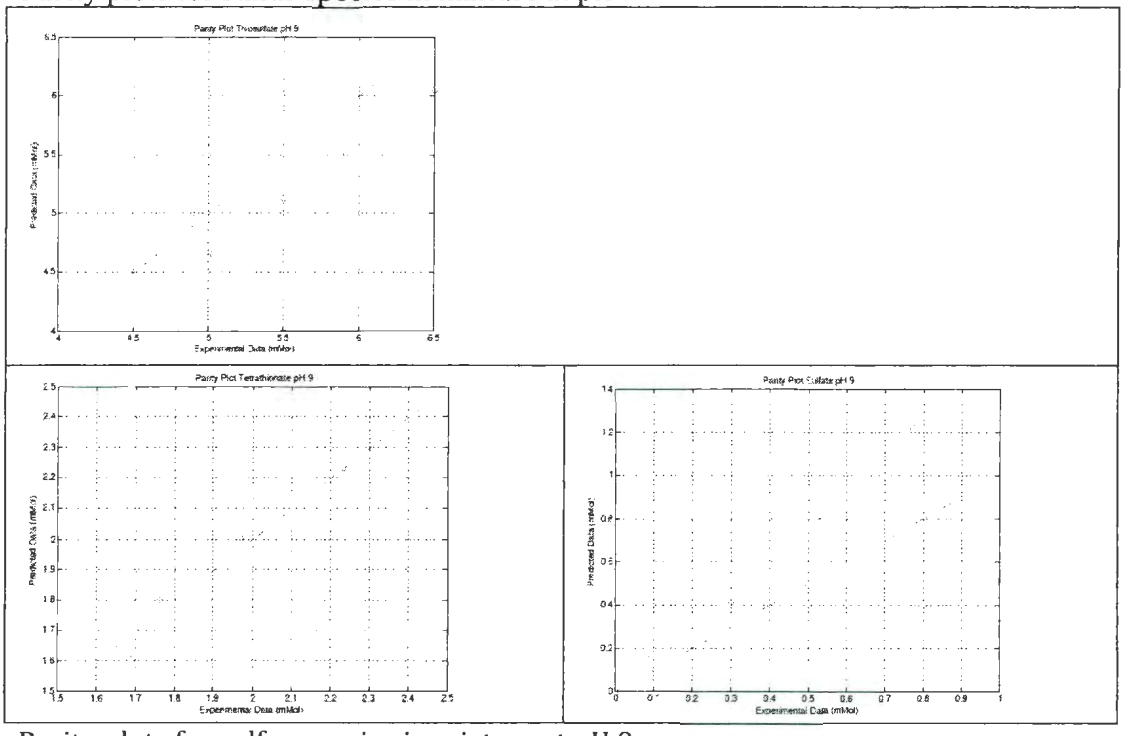


Parity plots for sulfur species in mixture at pH 4





Parity plots for sulfur species in mixture at pH 7

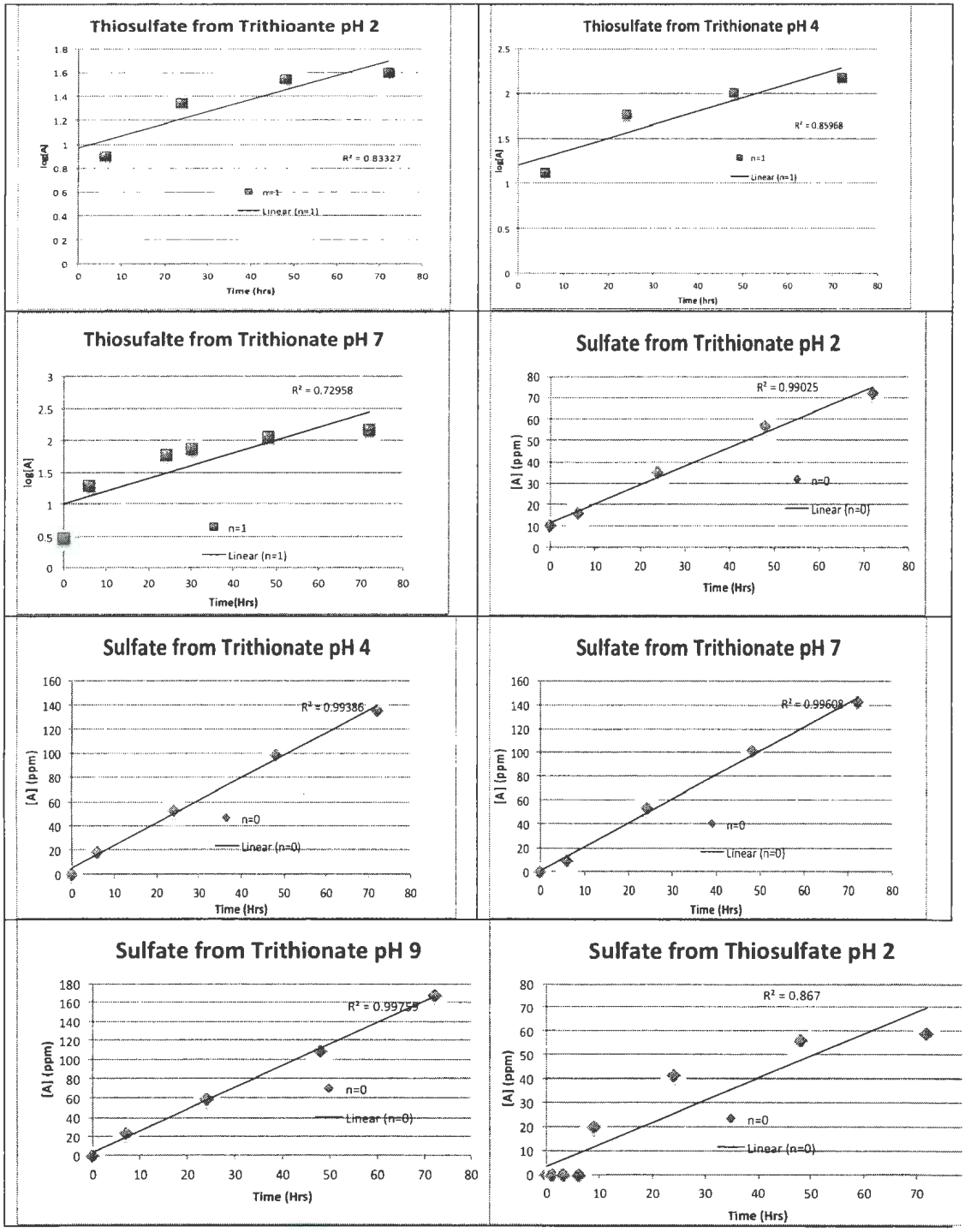


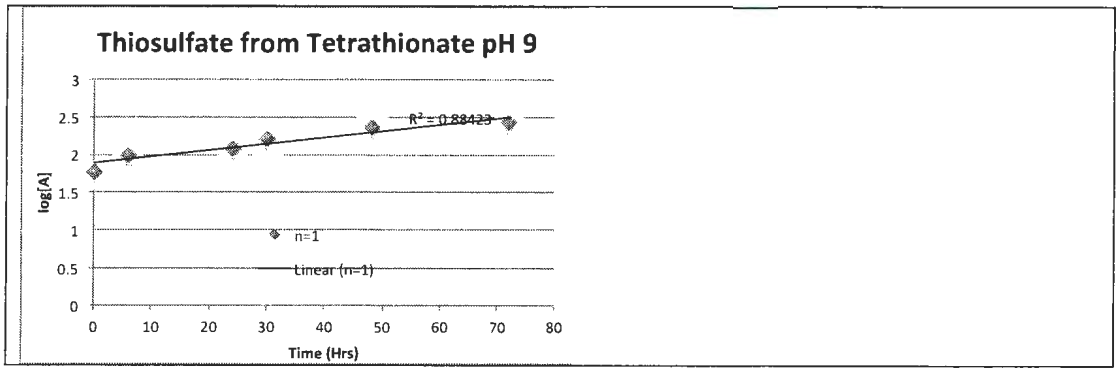
Parity plots for sulfur species in mixture at pH 9

A.5 Data for mixture reaction rates

pH 2 Temp 30 C				
time (hrs)	Thio (ppm)	Tri (ppm)	Tetra (ppm)	Sulfate (ppm)
0	500	500	500	0
9	355	577	431	0
24	277	574	436	11
30	285	572	397	14
48	242	523	452	38
72	261	537	429	47
pH 4 Temp 30 C				
time (hrs)	Thio (ppm)	Tri (ppm)	Tetra (ppm)	Sulfate (ppm)
0	500	500	500	0
6	507	505	470	0
24	530	483	450	24
30	539	482	437	
48	552	454	430	54
72	584	419	419	68
pH 7 Temp 30 C				
time (hrs)	Thio (ppm)	Tri (ppm)	Tetra (ppm)	Sulfate (ppm)
0	500	500	500	0
6	528	511	479	
24	571	502	445	30
30	542	472	430	
48	578	455	423	60
72	590	409	402	76
pH 9 Temp 30 C				
time (hrs)	Thio (ppm)	Tri (ppm)	Tetra (ppm)	Sulfate (ppm)
0	500	500	500	0
7	563	483	503	
24	551	485	441	29
30	616	497	423	
48	662	510	395	51
72	728	477	377	74

A.6 Van Hoff Plots for thiosalt mixtures




Thiosulfate from Tetrathionate pH 9
log[A]
Time (Hrs)
R² = 0.88423
n=1
Linear (n=1)
0
0.5
1
1.5
2
2.5
3
0
10
20
30
40
50
60
70
80

A.7 Matlab Optimization Models

Optimization of K and N without constrains

```
clc
clear

loadthiodata
Thiodata = Thiodata(:,2:end);  %get rid of column with the times
nCol = size(Thiodata,2);       %number of columns

K = 0:0.0001:0.1;           %range of K values
N = 0:0.1:3;                    %range of N values
nK = numel(K); nN = numel(N);     %array sizes
results = zeros(nCol,nK,nN); %matrix in which to store the error
results.

ICs = [250 250 250 500 500 500 1000 1000 1000];  %initial concentrations
Temps = [4 15 30 4 15 30 4 15 30];              %temp values


%Do exhaustive search and print results
fprintf('Best fits:\n\nTemp\tIC\t|\tK\t\tN\n');
for j = 1:nCol         %for each set of temp + IC data
for k = 1:nK
for n = 1:nN
F=@(t,y) -K(k)*y^N(n);
            [t,y]=ode45(F,[0 6 9 24 48 72],ICs(j));
results(j,k,n) = norm(y - Thiodata(:,j),2);  %compute least-square error
between data and model.
end
end

%for this set of data, search among the tested values of K and N for the
ones that gave the smallest error
tmpmat = squeeze(results(j,:,:));
    [m,ind] = min(tmpmat(:));
    [ind1,ind2] = ind2sub(size(tmpmat),ind);   %convert from one-
dimensional to 2-dimensional index

fprintf('%d\t%d\t|\t%.1e\t\t%.1e\n', Temps(j),ICs(j),K(ind1),N(ind2));
end
```

Optimization of K and N within a constrained range

```
clc
clear
loadthiodata2
thiodata2 = thiodata2(:,2:end);  %get rid of column with the times
datacol = 6;       %which column of data to fit
```

```
T = [0 6 9 24];
f = @(x) objfunc(x,T,thiodata2(:,datacol));  %anonymous function of one
variable (x)

x0 = [2.5e-4; 2];  %initial guesses for K and n, respectively

x1 = fminsearch(f,x0);                    %constrained minimization
fprintf('Best fit (unconstrained): K = %.1e\tn = %.1e\n',x1(1),x1(2));

x2 = fmincon(f,x0,[],[],[],[],[1e-8; 2], [4e-4; 2]);   %minimization
with constraints on K and n
fprintf('Best fit (constrained): K = %.1e\tn = %.1e\n',x2(1),x2(2));

%Plot results
K = x1(1); N = x1(2); IC = thiodata2(1,datacol);
odefun = @(t,y) -K*y^N;
[t,y1] = ode45(odefun,T,IC);

K = x2(1); N = x2(2);
odefun = @(t,y) -K*y^N;
[t,y2] = ode45(odefun,T,IC);

figure(1); plot(T,thiodata2(:,datacol),'k-',T,y1,'r-',T,y2,'b-
','LineWidth',2);
grid on; axis([0 T(end) 0.5*IC IC]); legend('data',sprintf('K = %.1e n =
%.1e\n',x1(1),x1(2)), sprintf('K = %.1e n =
%.1e\n',x2(1),x2(2)),'Location','SouthEast');
xlabel('Time (hrs)'); ylabel('Concentration');
```

objfunc

```
function res = objfunc(X,T,Y)
% Computes the solution to the ode y' = -Ky^N at the specified times T,
% and then compares it to the data specified in vector Y.

% X(1) is K, X(2) is N. Initial condition given by Y(1).

IC = Y(1); K = X(1); N = X(2);
   F=@(t,y) -K*y^N;
   [t,y]=ode45(F,T,IC);

res = norm(y-Y);
end
```

Graphs generation for pure species

```
clc
clear
%   Constants:
K=1e-4;
n=1.9;
loadthiodata
T= Thiodata(:,1);
%   Inputs for A concentration
datacol = 2; %column of data to fit
```

```
ICA=Thiodata(1,datacol);
%   Calculations
Thiomodel=@(t,y) -K*y^n;
[t,modelA] = ode45(Thiomodel,T,ICA);
SSEa=sum([Thiodata(:,datacol)-modelA].^2);
a=mean(Thiodata(:,datacol));
SSTa= sum((Thiodata(:,datacol)-a).^2);
R2a=1-(SSEa/SSTa)
%   Inputs for B concentration
datacolb = datacol+3; %column of data to fit
ICB=Thiodata(1,datacolb);
%   Calculations
thiomodel=@(t,y) -K*y^n;
[t,modelB] = ode45(thiomodel,T,ICB);
SSEb=sum([Thiodata(:,datacolb)-modelB].^2);
ab=mean(Thiodata(:,datacolb));
SSTb= sum((Thiodata(:,datacolb)-ab).^2);
R2b=1-(SSEb/SSTb)
%   Inputs for C concentration
datacolc = datacol+6; %column of data to fit
ICC=Thiodata(1,datacolc);
%   Calculations
thiomodel=@(t,y) -K*y^n;
[t,modelC] = ode45(thiomodel,T,ICC);
SSEc=sum([Thiodata(:,datacolc)-modelC].^2);
ac=mean(Thiodata(:,datacolc));
SSTc= sum((Thiodata(:,datacolc)-ac).^2);
R2c=1-(SSEc/SSTc)
% additional data for residual plot
resa= Thiodata(:,datacol)-modelA;
resb= Thiodata(:,datacolb)-modelB;
resc= Thiodata(:,datacolc)-modelC;
allres=[resa;resb;resc]
% data plot
figure(1); plot(T,Thiodata(:,datacol),'o',T,modelA,'r-
',T,Thiodata(:,datacolb),'o',T,modelB,'b-
',T,Thiodata(:,datacolc),'o',T,modelC,'b-')
figure (2); plot(allres)
```

Graphs generation for mixtures

```
clc
clear
loadMixph2t30
mw=112; %mw thio-112 tri-192 tetra-224 sulf-96
Data = unnamed(:,2:end);  %get rid of column with the times
Data = Data/mw;

datacol = 1;      %which column of data to fit (1-thiosulfate, 2-
trithionate, 3-tetrathionate, 4-Sulfate)

T = [0 9 24 30 48 72];
T1= [0:72];
E=(0.05*Data(:,datacol)); %6 for thio, 4 for tri, 9 for tetra, 5 for
```

```
sulfate

%Plot results for decay of thiosalt
K= -2.6e-2;
n= 2;
K1= 5.8e-2;
n1=1;
IC = Data(1, datacol);
odefun = @(t,y) K1*y^n1+K*y^n;
odefun2 = @(t,y) K*y^n;
[T1,y1] = ode45(odefun,T1,IC);
[T,y2] = ode45(odefun2,T,IC);

%Plot results for generation of thiosalt
%K = x1(1); N = x1(2); IC = Data(1, datacol);
%odefun = @(t,y) +K*y^N;
%[t,y1] = ode45(odefun,T,IC);

%K = x2(1); N = x2(2);
%odefun = @(t,y) +K*y^N;
%[t,y2] = ode45(odefun,T,IC);

%figure(1);plot(T1,y1,'r-')
%figure(3);plot(T,Data(:,datacol),'x');
errorbar(Data(:,datacol),E,'xb');
%figure(2); plot(Data(:,datacol),y2,'o',[0 1],[0 1],'r-'); grid on;
%xlabel('Experimental Data (mMol)'); ylabel('Predicted Data (mMol)');
title('Parity Plot Sulfate pH 2');
%figure(4);plot(T1,y1,'r-'); errorbar(T,Data(:,datacol),E,'x');
figure(1);plot(T1,y1,'r-',T,Data(:,datacol),'x',T,y2,'r--');
gridon; axis([0 75 0 5]);
xlabel('Time (hrs)'); ylabel('Concentration (mMol)'); title('Thiosulfate
in Mixture pH 2'); legend('Simulation - Mixture', 'Experimental Data',
'Simulation - Pure Species');
```